

STANDARDS DEVE. GRMEN 1 BRANCH OMUL
3693600005659

ACIDIC PRECIPITATION IN ONTARIO STUDY

AN ANNOTATED BIBLIOGRAPHY

TERRESTRIAL EFFECTS OF ACIDIC PRECIPITATION

APIOS 003/81

FALL 1981

TD
195.54
.06
A56
1981
3701



Ministry
of the
Environment

The Honourable
Keith C. Norton, Q.C.,
Minister
Gérard J. M. Raymond
Deputy Minister

TD
195 54
06
A50
1981

ACIDIC PRECIPITATION IN ONTARIO STUDY

AN ANNOTATED BIBLIOGRAPHY

TERRESTRIAL EFFECTS OF ACIDIC PRECIPITATION

Edited by: S.N. Linzon, Ph.D.

Vegetation Section: prepared by W.I. Gizyn, M.Sc.

Soils Section: prepared by M.A. Griffith, M.Sc.

PHYTOTOXICOLOGY SECTION

AIR RESOURCES BRANCH

880 Bay Street, 3rd floor

Toronto, Ontario

M5S 1Z8

APIOS Report

No. 003/81

APIOS Co-ordinator - Mr. E. Piche

40 St. Clair Avenue West, 6th Floor

Toronto, Ontario

M4V 1M2

Copyright Provisions and Restrictions on Copying:

This Ontario Ministry of the Environment work is protected by Crown copyright (unless otherwise indicated), which is held by the Queen's Printer for Ontario. It may be reproduced for non-commercial purposes if credit is given and Crown copyright is acknowledged.

It may not be reproduced, in all or in part, part, for any commercial purpose except under a licence from the Queen's Printer for Ontario.

For information on reproducing Government of Ontario works, please contact Service Ontario Publications at copyright@ontario.ca

TABLE OF CONTENTS

Introduction	1
Effects on Vegetation	2
Effects on Soil	73
Reviews and General Papers	158
Popular Press Articles	178
Senior Author Index	180

INTRODUCTION

This bibliography, we believe, is the first attempt to bring together all the scientific literature on the effects of acidic precipitation on terrestrial ecosystems. It is different from other bibliographies in that it is annotated, that is, in addition to listing the available literature, the information provided in each article is summarized and reviewed. The articles are grouped into main divisions, as effects on vegetation and effects on soils, and further subdivided into theme topics with the articles listed alphabetically by authors in each subgroup. Further, this bibliography excludes papers dealing with the precursor pollutants as sulphur dioxide and nitrogen oxides alone unless there is direct reference to their contribution to acidic precipitation and effects on terrestrial systems. Those articles dealing with aquatic effects alone are not referred to in this bibliography.

The literature on terrestrial effects of acidic precipitation available to us by the end of 1980 are included in this bibliography. It is anticipated that supplements will be produced from time to time. A copy of every paper listed in this bibliography is stored in the Terrestrial Effects Working Group reference file located on the third floor at 880 Bay Street, Toronto.

The purpose of assembling the available literature on terrestrial effects is to lay the foundation for future work and to make available to the reader the present state of knowledge in this highly important area of research.

VEGETATION SECTION**Table of Contents**

A)	Vegetation Injury - Symptomatology	3
B)	Tissue Leaching by Acidic Precipitation Simulants	20
C)	Throughfall Chemistry - Canopy Interactions	26
D)	Effects on Growth and Productivity	41
E)	Effects on Plant Reproduction	56
F)	Host-Parasite Interactions and Nitrogen Fixation	60
G)	Miscellaneous - Vegetation	65

A.

VEGETATION INJURY - SYMPTOMATOLOGY

The most common approach to test for the effects of acidic precipitation on plants has been to treat plants with acidic solutions as simulants of acidic precipitation. The treatments have varied considerably in frequency, intensity, application method, ambient conditions, acidity and solution chemistry. This makes it very difficult to make comparisons.

Effects observations have concentrated on foliar injury symptomatology but have also included observations of morphological and physiological perturbations. Effects begin to appear when treatment pH is in the vicinity of 3.5 and lower. No confirmed effects on vegetation have been reported under ambient conditions attributable to rainfall acidity.

(1) Foliar Responses That May Determine Plant Injury by Simulated Acid Rain
L.S. Evans; In: Polluted Rain, T.Y. Toribara, M.W. Miller and P.E. Morrow (eds), Plenum Press, New York, 1980, pp. 239-257.

The research described was designed to predict relative sensitivities of various plant species to simulated acid rain. Organisms will not respond in an identical manner to abiotic or biotic influence. It is hoped that the response of one species as reflected by cell or tissue alterations can be used to predict relative sensitivities of other species.

This paper is an integration of other papers by Evans and his co-workers on the subject of injury symptomatology to acidic rain simulants. (Evans and Curry 1979, Evans et al 1977, 1978.) Details of these experiments have been summarized in this bibliography and will not be repeated here except to note that acidified solutions were applied to foliage of test species.

A table listing the test species together with observed percent of leaf area injured under various treatment regimes is presented. In an accompanying discussion it is noted that oak was the least sensitive species tested. Spiderwort and poplar were intermediate although in the case of poplar, the areas that developed galls were included. Soybean, sunflower, pinto bean and bracken fern exhibited the most injury.

A relationship between sensitivity and leaf age was established in pinto beans. Lesion density was lowest in leaves prior to the period of maximum rate of expansion. The stage at which the leaves had the greatest density of stomata and trichomes was not the most sensitive stage. Young soybean leaves were more sensitive than fully expanded leaves. Leaves rapidly expanding or recently

expanded are most sensitive. Very small, immature and older leaves are less sensitive. The reason for this relationship is unknown.

In most of the test species, about 75% of lesions were localized near veins. Lesions were also located primarily near trichomes (75%) and stomata (20%). Once a lesion developed, it expanded with subsequent treatment. The lesion forms a depression for pooling of acidic solution.

Test species were examined histologically to determine how injury progressed at this cellular level. See the appropriate summaries elsewhere in this bibliography.

In a general conclusion, the author used data of others to suggest that coniferous species are less sensitive to injury by acidic rain solution than are broad leaf woody plants. Broad leaf herbaceous plants are most sensitive. Initial response of plants may be governed by characteristics of the leaf surface. However, once epidermal cells are injured, plants that exhibit hyperplastic or hypertrophic response (galling) may avoid additional injury.

(2) Differential Responses of Plant Foliage to Simulated Acid Rain

L.S. Evans and T.M. Curry; American Journal of Botany, Vol. 66, 1979, pp. 953-962

Simulated rain at pH 5.7, 3.4, 3.1, 2.9, 2.7, 2.5 or 2.3 was applied daily for 20 minutes to Glycine max (soybean), Tradescantia sp, (spiderwort), Quercus palustris (pin oak) and Pteridium aquilinum (bracken fern). (2 times per day for spiderwort). Lesions were categorized according to diameters. Histological sections were examined.

Injury symptoms on the plants are described extensively. In general, lesions developed in a sequence on plant tissue. Decreasing the rain pH and repeating the exposure produced more lesions and more injury within a lesion. Whereas gaseous pollutants affect mesophyll first, acid rain affected leaf surfaces. Vascular tissue and cells at trichome bases form natural depressions in the leaf surface permitting pooling of rain water and are sites of injury. Evaporation of acidic water will concentrate the acid.

The different species exhibited diverse responses to acidic solutions. Fern pinnae epidermal cells were initially affected and injury progressed to internal tissue. Necrotic epidermal cells create a depression for accumulation of subsequent rain. Pin oak exhibited hypertrophy and hyperplasia in mesophyll cells. Protrusions appeared on the adaxial surface adjacent to lesions. Xylem and phloem cells were the only cells not affected.

From data presented in this work, as well as from other publications,

differential sensitivities of plants to acid rain are discussed. Injury to fern, bean and sunflower was similar, with lesions appearing 24 hours after the first response to pH 2.7 and 2.5 rain. While poplar is injured after 3 daily 6 minute exposures at pH 2.7, pin oak is not injured until 13 daily exposures at pH 2.5. Bracken fern is the most sensitive to acid rain.

Foliage of broad leaf trees appears to be more sensitive to acid than conifer needles, while herbaceous plant foliage is more sensitive than tree foliage. The relative insensitivity of pin oak may be due to the hypertrophic/hyperplastic response elevating tissue and preventing pooling at the injury site.

While leaf indumentum characteristics may determine the site of initial injury, response of tissue, such as hypertrophy and hyperplasia may alleviate extensive injury.

This publication synthesizes much of the work that has been done on acid rain symptomatology. Sensitivity is related to foliage characteristics.

(3) Leaf Surface and Histological Perturbations of Leaves of Phaseolus vulgaris and Helianthus annuus after Exposure to Simulated Acid Rain

L.S. Evans, N.F. Gmur and F. DaCosta; American Journal of Botany, Vol. 64, 1977, pp. 903-913

Bean and sunflower plants were exposed to simulated rain, with pH adjusted by H_2SO_4 , daily for 6 minutes at a rate of 7.2 mm/hr. pH of test solutions were 5.7, 3.1, 2.9, 2.7, 2.5 and 2.3. Leaf tissue was examined by histological cross section and S.E.M. Density of stomata and trichomes was measured.

Initial experiments (6 minutes of "rain" every 3 days) showed that sunflower at the 3-4 leaf stage was more sensitive to acidic rain than at older stages. No such differences were noted for bean. Total area of injury increased with repeated exposure for acid.

Plants exposed to the acid daily were examined extensively and degree of injury categorized according to size and extent of lesions, chlorosis, cells affected and leaf stage affected. Development and progression of injury is extensively described and is based primarily on observations from the pH 2.7 treatment.

Unlike injury caused by gaseous pollutants, acid rain first affects epidermal cells. Lesions are localized but enlarge with subsequent exposures, collecting in the injury induced depressions. Injury progresses to underlying cells.

Bean plants do not show a relationship of degree of injury to age. Only very young unexpanded leaves are less sensitive despite the higher density of stomata and trichomes. Injury does, however, occur primarily in association with these

structures. This suggests that epidermal cell morphology during development predisposes leaves to injury. Species sensitivity differences to acid rain may be influenced by characteristics of leaf indumentum.

This work has an extensive description of the injury symptoms based on observations with the daily pH 2.7 treatment. Considerable emphasis is placed on characteristics of the tissue damage and how it relates to leaf surface morphology.

(4) Foliar Response of Six Clones of Hybrid Poplar

L.S. Evans, N.F. Gmur and F. DaCosta; *Phytopathology*, Vol. 68, 1978, pp. 847-856

Six hybrids of poplar (Populus spp) were sprayed from above with simulated acid rain with pH adjusted by H_2SO_4 to 2.7, 2.9, 3.1, 3.4 and 5.7. Cuttings were rooted in soil. Exposure was for 6 minutes daily at a rate of 7.2 mm/hr. Injury was examined histologically and by S.E.M.

At "rain" pH 5.7 no injury was observed while several clones exhibited small lesions (1.0 mm) at pH 3.4 one day after the fifth treatment. Area of leaf tissue injured and number of lesions increased with number of treatments and with increasing acidity. Small (0.25 mm) lesions occurred after 1 treatment at pH 2.7 or 2.9. Chlorosis was followed by necrosis. Large lesions developed in a circular pattern while some clones exhibited a red coloration at lesion peripheries. Lesions were initially localized near stomata and vascular tissue.

Two clones also developed galls. Palisade and spongy parenchyma cells exhibited hypertrophy and hyperplasia (cell enlargement and proliferation) after collapse of adaxial epidermis, resulting in elevated leaf surfaces.

Although lesions developed near stomata, there was no correlation between density of adaxial stomata and density of lesions. Lesions were more frequent, however, on leaves undergoing expansion.

Comparison of Populus responses to acid rain to that of bean and sunflower (Evans et al 1977) suggests poplar to be more sensitive (more lesions for given treatment acidity). Conifers did not exhibit symptoms above pH 2.5 "rain" (Evans unpublished). Deciduous tree areas are more threatened than coniferous areas.

The features of deciduous tree and crop plant foliage determining sensitivity is unknown. While lesions appear primarily near stomata and trichomes, density of these features and lesions are not correlated. A temporary decrease in cuticle thickness (during leaf expansion) may relate to sensitivity at this stage.

Lesion development proceeded to enlarge the necrotic area to a final diameter of several millimeters after several exposures. Frequency of lesions continued to increase. Depth of lesions progressed from adaxial to abaxial

surfaces.

Differential sensitivity of species may be influenced by characteristics of leaf indumentum, as occur near stomata, trichomes or vascular areas.

The observation of galling in this work suggests a response at the physiological level. This would require some degree of toxin translocation.

(5) Perturbations of Upper Leaf Surface Structures by Simulated Acid Rain
 L.S. Evans, N.F. Gmur and J.J. Kelsch; Environmental and Experimental Botany,
 Vol. 17, 1977, pp. 145-149

Phaseolus vulgaris (bean) and Helianthus annuus (sunflower) were used to examine foliar injury induced by simulated acid rain application. "Rain" was acidified by H_2SO_4 to pH of 5.7, 3.0 and 2.7 and applied at a rate of 0.78 cm/hr, daily for a 6 minute period. Leaves were examined under a scanning electron microscope 24 hours after daily and cumulative exposures.

Initial injury consisted of a localized collapse of adaxial epidermal cells. More cells became injured after cumulative exposures to acidic solutions. Such lesions occurred primarily in epidermal cells adjacent to trichomes (75%) and stomata (20%).

Liquid water can penetrate stomata and liquid water exchange can occur via hydathodes (trichomes). These structures excrete water and salt and so the cuticle may be thin or removed; thus permitting rapid liquid movement including penetration of acidic rain. Injury to foliage may explain accelerated nutrient leaching.

This paper presents some theories for site specific damage by acidic rain. A tangible explanation may be the simple collection of rain drops at these morphological structures of leaves.

(6) Effects of Simulated Acid Rain on Phaseolus vulgaris L. (Fabaceae)
 R. Ferenbaugh; American Journal of Botany, Vol. 63, 1976, pp. 283-288

Phaseolus vulgaris (bean) plants were sprayed daily with distilled water acidified with H_2SO_4 until leaves were thoroughly wetted. Solution pH's were 5.5, 4.5, 3.5, 3.0, 2.5 and 1.5. Histological, physiological and biochemical perturbations were assessed.

At pH 2.5 and lower, plants exhibited shorter internodes and increased bud formation. Leaves were smaller with rolled-under margins. At pH 2.0 and 1.5,

necrotic spots appeared and leaves abscised prematurely. At pH 2.5 and less, leaves had smaller cells and less intercellular space. Starch granules within chloroplasts were also smaller and epidermal cells and bundle sheath parenchyma were acidified below pH 4.0.

Chlorophyll content of tissue was significantly reduced at the pH 2.0 treatment but this was likely due to the high incidence of necrosis at this treatment. Acid treatment increased the apparent rate of photosynthesis (O_2 consumed/unit weight of tissue). Sugar and starch content also decreased at pH 2.5 compared to control (pH 5.5).

Biomass, especially of roots was significantly reduced at the pH 2.5 treatment.

A proposed mechanism for the stunted growth and abnormal leaf development is by an acid-auxin interaction. Auxin synthesis has acid sensitive intermediates. While biomass and carbohydrate data suggest the plants lose carbohydrate production capacity, there is an increase in apparent rate of photosynthesis. Slight increases in respiration would be insufficient to metabolize the extra carbohydrate. The uncoupling of photophosphorylation is suggested as a possibility for producing high photosynthetic rates while reducing carbohydrate production.

Similar increases in photosynthesis were observed when leaf tissue was immersed in HCl solution. Acidity and not $SO_4^{=}$ ions are responsible for observed effects.

Prior to selection of the beans for experimentation, Chenopodium quinoa (pigweed) and Hordeum vulgare (barley) were tested but showed no immediately discernable response. This differential species susceptibility may alter plant community composition and natural food chains. Food production may be reduced.

The number of acid solution applications is not given. Since plant biochemical processes operate at an optimal cellular pH, acidification of cell contents will alter physiological processes, affecting productivity.

(7) Conifer Tree Damage in the Vicinity of Large Stationary Sources of Phytotoxic Gases: Mount Storm, West Virginia and Other Areas of the United States

C.C. Gordon and P.C. Tourangeau; Paper #75-21.1 presented at 68th Annual Meeting of the Air Pollution Control Association, Boston, Mass., June 15-20, 1975

Plantations of conifer trees began to exhibit unusual damage not reported from any other location. Three coal fired power plants located within a 50 mile

radius of the plantations in the Mount Storm area were suspected as emitters of the causal agent.

Two types of plant damage were apparent. The first comprised of random dwarfing of needles and excessive or lack of development of dwarf shoot buds. The second comprised a premature drop of second and third year needles. Such a combination of symptoms was unknown to be caused by air pollution.

It was hypothesized that since biotic agents were unlikely to cause such injury, the agent was abiotic. Acidic or alkaline precipitation or airborne particulates with acidic or alkaline properties when moistened were investigated.

Simulated rain acidified by H_2SO_4 , HF or HNO_3 (pH range 1.5 to 5.5) NaOH and KOH solutions (pH 10.5 to 12.0) and fly ash as a slurry or as a dust were applied to pine seedlings. Biotic agents and rainfall samples collected in the Mount Storm area were investigated.

Results of the simulated rain application experiments with the acid solutions revealed histological symptoms and growth abnormalities identical to those seen in the field. The less acid solutions required a longer duration of exposure to produce symptoms.

Alkaline rain, fly ash application and biotic agents were ruled out as causal agents for the particular symptoms.

The histology of the damaged needles is extensively described but the general conclusion is that acidic precipitation runs down the needles and accumulates at the fascicle base. After penetrating the needles the acid causes lesions and induces growth abnormalities. It is stressed that such effects have not been documented before because the primary site of injury occurs beneath the sheath covering the needle base.

Such damage can occur when rainwater with a pH below 5.0 to 4.5 collects between the fascicle sheath for an extended time. Increasing prevalence of acidic precipitation poses a threat to forests and horticultural species.

The paper purports that acidic rainfall now occurring has damaged vegetation. It is therefore distinct from reports of damage using simulated rain of unrealistically low pH. The argument could have been strengthened if there was evidence of a correlation of low pH rain and onset of symptoms, or if there was some observations as to the duration for which the acid rain remained beneath the fascicle sheath. Evidence of acid based salt accumulations with the sheath would add to the argument, since neutralization of the acid would be occurring.

(8) Growth Abnormalities of Christmas Trees Attributed to Sulfur Dioxide and Particulate Acid Aerosol

I.J. Hindawi and H.C. Ratsch; Paper #74-252 presented at 67th Annual Meeting of the Air Pollution Control Association, Denver, Colorado, June 9-13, 1974

Needle discoloration of Scotch pine, typical of SO_2 and/or O_3 injury were reported. Additional growth abnormalities included short needles, premature needle drop, bud failure and stunted growth. Causes of these symptoms were investigated.

Needle tip burn of Scotch, white and Austrian pine were observed in the vicinity of a coal burning power plant and attributed to SO_2 . Subsequently, (next year) Scotch pine previously injured by SO_2 displayed short needles interspersed with normal needles.

Tobacco, pinto bean, petunias and Scotch pine were grown in field chambers with and without air filtration. No injury was recorded for filtered air plants while damage to tobacco, pinto bean and petunia in unfiltered air was attributed to SO_2 and O_3 . Damage to Scotch pine consisted of short needles, growth suppression, tip burn and yellowing could not be ascribed to a specific pollutant.

Reciprocal transplantation of trees between damaged and non-damaged sites was performed. Movement of healthy trees into the damage prone area induced the short needle syndrome, while movement of damaged trees out of this area induced recovery. Similar results were obtained when scions (grafts) were transplanted.

Scotch pine seedlings were exposed to acid mist of different pH (1.5 to 6.8) and at different frequencies (daily to weekly) in the field. Short needles and tip injury occurred at mist pH 2.0 (versus 6.8) with daily misting. Shorter needles appeared with alternate day misting by pH 2.0 and 3.0 solutions. Differences in needle length were not significantly different from higher pH mist applications. Weekly misting with pH 1.5 mist resulted in significantly shorter needles.

Examination of the short needles revealed a sunken area beneath fascicle sheath. Microscopic examination revealed plasmolized epidermis and swollen mesophyll cells. Tissue in other sections of short needles were normal.

Acid mist present on terminal bud scales prior to needle elongation causes short needle formation. Penetration of the fascicle sheath, needle epidermis and mesophyll layer injures the cambium and results in reduced needle elongation.

It is concluded that the injurious effects seen near the high fume emission sources are due to gaseous pollutants. Acid mist also caused tip injury and short needle formation. It is suggested that sulphuric acid formed when dew saturates the fly ash (reviewer's note: H_2SO_4 forms when SO_2 saturates the dew; editing

error suspected in original text). Deterioration of needle bases before or during the elongation period results in shortened needles.

Since misting was conducted in the field, ambient gaseous pollutant concentrations were not controlled during the experiments. Insufficient experimental controls were utilized in this investigations and leave some doubt regarding the conclusions.

(9) Response of Bush Bean Exposed to Acid Mist

I.J. Hindawi, J.A. Rea and W.L. Griffis; Paper #77-30.4 presented at 70th Annual Meeting of the Air Pollution Control Association, Toronto, Ontario, June 20-24, 1977

Phaseolus vulgaris (bush bean) plants were subjected to mists consisting of dilute sulphuric acid and other ions (simulated rain) at pH 5.5, 4.0, 3.0, 2.5 and 2.0. Two week old plants were misted weekly for 6 weeks for 45 minutes at a rate of 0, .006, .06, .02 and .6 ug $H_2SO_4/cm^2/min$ (corresponding to the pH levels). Additional plants were exposed to mist 5 times per week.

Subsequently, leaves were examined for injury. Chlorophyll, N, P, Ca, Mg and K concentration was determined. S was determined for plants under the more frequent misting regime.

Visible symptoms occurred on plant treatments of pH less than 3.0. Symptoms progressed from incipient bronze spotting within hours of misting to bifacial lesions by the following day. Microscopic examination of injured tissue showed loss of chloroplast integrity and plasmolysis of palisade cells. In severe cases, epidermis and spongy mesophyll were damaged.

Productivity (as dry weight) was progressively reduced for vegetative and reproductive tissue as acidity increased. Plants receiving pH 2.0 treatment had a 33% reduction in leaf tissue mass, compared to pH 5.5. Productivity was reduced even if no injury was apparent. Chlorophyll concentration was reduced with increasing acidity, with pronounced reduction at pH 2.5.

Foliar concentrations of N, Ca, P and Mg declined with increasing acidity while K was unaffected. S concentration was higher in the pH 2.0 treated plants (intense misting) and also in the soil. Soil Ca and K were not affected.

While foliar injury is undoubtedly responsible for reduced productivity, significant reductions can occur without injury. Simple destruction of photosynthetic tissue is not the only mechanism responsible. Macronutrient concentration reduction in tissue may relate to reduced productivity but the concentrations were still adequate. Ferenbaugh's (1976) suggestion of H^+ ion

induced uncoupling of phosphorylation is cited. Reduced weight of pods yet no reduction in number of pods produced suggests a reduction in carbohydrate production by affected leaves. Reduction of foliar concentrations of Ca, P, and Mg may result from leaching losses, disruption of root uptake mechanism and acid hydrolysis of chlorophyll resulting in Mg loss.

(10) Interaction of Acid Precipitation and Forest Vegetation

R. Horntvedt, G.J. Dollard and E. Joranger; Mimeographed summary of a paper presented at IUFRO Air Pollution Meeting, Sept. 1 - 6, 1980, Graz, Austria

This paper is a brief summary of experimental results and field observations made within the Norwegian SNSF project. The relevant SNSF reports are summarized elsewhere in this bibliography.

Some new information is presented here however. Conifer needles subjected to the acid irrigation experiments were examined for loss of cuticular wax. No such loss could be seen either by scanning electron microscope for plants treated by pH 2.5 solutions or by chloroform extraction and evaporation and weighing of needle waxes.

The results of some wind tunnel experiments conducted to measure dry deposition of SO_2 are also presented.

(11) Induction of Visible Injury in Chamber-Grown Soybeans Exposed to Acid Precipitation

P.M.Irving; In: Radiological and Environmental Research Division Annual Report, Argonne National Laboratory, Argonne, Illinois, Jan.-Dec., 1978, ANL-78-65, Part III, pp. 24-25

Response of plants to acid precipitation will depend on acidity of precipitation and quantity of acid rain.

Eight groups of soybean plants were exposed to a range in quantity (0.65 to 9.35 cm) of pH 3.0 and 5.6 simulated rain within a four day period. Rate of application was 2.7 cm/hour. Damage was not visible with the pH 5.6 rain treatment.

Lesions and chlorotic areas were observed at the pH 3.0 level. Lesions occurred with as little as 2.0 cm of pH 3.0 rain and all plants showed damage after 7.0 cm of rain over 3 days. 10 days after exposure to the highest quantity of rain, chlorotic areas appeared in 40% of the plants.

Necrotic areas did not exceed 5% of leaf area, while chlorosis covered up to 25% of the leaf area. Since damage occurred only on specific leaves, tissue damage of the whole plant was negligible and photosynthesis of the plant would not be reduced. New growth appeared normal after rain applications ceased.

High exposure rates at lower than naturally occurring rain pH is required to produce significant damage.

Specificity of damage ie. on leaves of specific age is interesting but not discussed. Chlorosis suggests that damage by acid rain can include symptoms other than localized necrotic lesions and implies translocation of a toxic agent.

(12) Experimental Studies on the Phytotoxicity of Acidic Precipitation: The United States Experience

J.S. Jacobson; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 151-160

Changes in components of the terrestrial ecosystem as a result of acid precipitation are suspected but are unproven. The response of vegetation to direct contact with acidic precipitation is being investigated at laboratories in the United States and some of this work is examined.

It is assumed by most investigators that H^+ ions are the most likely component of rain to be harmful. Sulphate, nitrate, chloride, ammonium, calcium, magnesium, sodium and potassium ions are benign or beneficial at concentrations encountered in precipitation. It has been observed that occurrence of foliar symptoms were not altered by additions of such ions as long as pH was unchanged.

The most frequently reported response to acidic precipitation in simulation experiments is the formation of lesions on leaves due to injury of cells. Cuticle erosion, gall formation due to cell proliferation or enlargement, premature leaf abscission and reduced photosynthesis have been observed. While leaching of elements from leaves has been observed, changes in foliar concentrations have not.

Beneficial effects are possible when nutrients in the acidic precipitation benefit nutrient deficient plants.

Stage of foliar development and cuticular features will regulate response. Herbaceous species appear highly sensitive to formation of lesions, while deciduous tree foliage is more susceptible than conifer foliage.

Duration, frequency and intensity of acid precipitation events will influence foliage symptoms. Interactions with gaseous air pollutants are being investigated.

In defining a threshold of acidity for phytotoxic effects, it is necessary to consider the dose-response relationship which considers acidity level, duration and

frequency of exposure. Detectable foliar lesions occur when simulated rain of pH 3 to 4 is applied.

Efforts to discover the full range of effects of acidic precipitation and factors which interact must continue. Susceptibility of organs other than leaves should be examined as should processes of vegetative growth.

This paper summarizes research conducted relating to direct effects of acidic precipitation on vegetation. Most of the literature cited is reviewed more extensively in this bibliography.

(13) Effects of Acidic Precipitation on Vegetation

J.S. Jacobson and P. van Leuken; In Proc: 4th International Clean Air Congress, Tokyo, Japan, 1977, pp. 124-127

An experimental study of the effect of simulated acidic rain on greenhouse and field grown conifers and herbaceous vegetation was conducted to; 1) demonstrate typical foliar symptoms; 2) estimate acidity threshold for response under experimental conditions; 3) determine what chemical factors other than H^+ ion concentration are likely to alter the appearance of foliar symptoms.

Pinus strobus (Eastern white pine), P. sylvestris (Scotch pine), Helianthus annus (sunflower), Phaseolus vulgaris (bean) and Spinacea oleracea (spinach) were sprayed with simulated rain.

The rain solutions were dilute nitric and sulphuric acid, simulated rain solution or acidified ambient rain. pH of solutions was adjusted by H_2SO_4 and HNO_3 to a range of 2.2 to 3.4. Treatment periods ranged from 1 minute to 9 hours using various application, intensity and frequency regimes. Plants were examined for injury following completion of treatment(s).

Symptoms consisted of necrotic lesions. No growth or development abnormalities were observed. On pine, lesions developed at the apical and mid-portion of needles. In severe injury whole needles became discoloured and abscission was early. Injury occurrence varied from tree to tree, within trees and within fascicles. Dormant conifers were tolerant while injury developed more readily on older needles. White pine was more susceptible than Scotch pine. Greater acidity was required to injure pine than to injure herbaceous species.

On unifoliate leaves of bean, lesions occurred where droplets had adhered, were scattered over the leaf and were tan to dark brown. Severity of injury varied. Symptoms on sunflower and spinach leaves consisted of light brown irregularly shaped lesions.

Foliar injury to herbaceous plants increased with increasing treatment time

and acidity. Injury was induced at pH 2.6 after one minute, at pH 3.0 after 1.5 hours, at pH 3.2 after 3 hours and at pH 3.4 after 9 hours.

The presence of other ions did not alter appearance of symptoms or their frequency on herbaceous plants. Repeating treatments, extending duration of treatment, increasing intensity of treatment and reducing period between treatments increased injury.

No aberrant growth or development was observed in conifers. Necrosis is the typical response to acidic rain.

A relationship between treatment duration and pH is drawn. It shows that long duration at a pH as high as 3.4 can produce necrosis of herbaceous species. Herbaceous species are more susceptible than conifers.

Duration, frequency and intensity of rain will influence foliar response to H^+ ions. Other ions do not appear to have an influence as long as pH is held constant.

Other implications of acidic rain to vegetation that were not assessed here involve growth and yield reduction after prolonged and repeated exposure to acid, leaching of elements from leaves, host-parasite relation alterations and effects in soil fertility. Such effects may be more important than foliar injury.

While present ambient rain pH is below the threshold for injury, the risk of surpassing this threshold for sensitive species is present.

Extensive details of treatment regimes and responses of species are not given. Selected observations are presented to give an overall view of the response of vegetation to acidic precipitation.

(14) Injury to Vegetation Incited by Sulfuric Acid Aerosols and Acidic Rain

D.S. Lang, S.V. Krupa and D.S. Shriner; Paper #78 - 7.3 presented at 71st Annual Meeting of the Air Pollution Control Association, Houston, Texas, June 25 - 30, 1978

Two series of experiments are described and discussed in this paper. The first addresses injury symptomatology of several species under an exposure to submicron aerosols of sulphuric acid in chambers. Differential susceptibility was noted. It was also proposed that the fine aerosols behave like a gas, being translocated within the leaf.

The second experiment was designed to view the effect of simulated acidic rain on willow oak. Young seedlings, planted in a potting mixture, were exposed to either deionized water (pH 6.0) or deionized water acidified to pH 3.2 with H_2SO_4 . Treatment occurred in a greenhouse. Simulated rain was applied daily for 10 minutes (0.63 cm) for 60 days.

On a macroscopic scale, numerous, small (1 mm) bifacial lesions were observed on the pH 3.2 treated plants. Scanning electron microscope examination of leaves of equal developmental status revealed microscopic differences for different treatments. Plants which were treated with the pH 3.2 solution had obvious erosion of cuticle surface waxes. The pH 6.0 treated plants had less surface wax than plants not exposed to any spraying.

The significance of eroding cuticular wax was discussed. Transpirational losses may be enhanced and leaf surface wettability is increased. The loss of water repellancy may predispose plants to waterborne pathogen inocula. The reduction in wax thickness may also enhance foliage leaching losses. Loss of cuticle wax may also predispose the plant to various pathogens and insects and reduce resistance to frost and ultra-violet radiation.

It is emphasized that plants grown in the field will have thicker cuticles and consequently one can only speculate as to related effects of acidic precipitation on plants in the field.

(15) The Effect of Hydrogen Ion Concentrations in Simulated Rain on the Moss Tortula ruralis (Hedw.) Sm.

R.P. Sheridan and R. Rosenstreter; The Bryologist, Vol. 76, 1973, pp. 168-173

Mosses are important colonizers of soil and depend on rainwater for moisture. Since rain falling on moss will be unbuffered by soil bases, mosses may be useful organisms for examining biological effects of acidity in rain.

The moss Tortula ruralis was maintained in petri dishes and sprayed with experimental solutions every 48 hours, for 8 treatments. Solutions were distilled water and dilute H_2SO_4 , covering pH range 1 to 6. Following treatment, rates of photosynthesis and respiration were measured and chlorophyll content determined.

Chlorophyll concentration declined uniformly between pH 6 and 3 and more rapidly between pH 2 and 1. A yellow-green appearance occurred at pH 3, increasing with decreasing pH. The ratio of chlorophyll a to b declined with increasing acidity indicating chlorophyll a to be more sensitive to the acid.

The rate of photosynthesis (O_2 evolved) based on unit of chlorophyll remained constant down to pH 2 but declined rapidly below 2.

On a unit weight basis, photosynthesis decline parallels decline of chlorophyll. Respiration rate (O_2 consumed) remained constant between pH 6 and 2 but declined rapidly below pH 2.

Photosynthesis is affected through a reduction in chlorophyll content and not through inhibition of photosynthetic mechanism. Acid hydrolysis of chlorophyll,

especially chlorophyll a is probably the mechanism by which photosynthesis rate is reduced.

It is shown that the chlorophyll a content and photosynthesis has begun to decline when the pH is lowered to pH 5. Rainwater pH lower than this is common and it may mean that plants dependant on the atmosphere for moisture and nutrients would be especially sensitive to rain acidity.

(16) Simulated Acidic Precipitation Causes Direct Injury to Vegetation

D.S. Shriner; Proceedings of the American Phytopathological Society (Annual Meeting, 1974), Vol. 1, 1975, p. 112 (abstract)

Seedlings of Pinus strobus, Quercus phellos, Phaseolus vulgaris and Glycine max were exposed to a simulated sulphuric acid rain (pH 3.2) in the greenhouse or field. Seedlings of Pinus taeda were exposed to "rain" of pH 1.9 to 6.1.

All plants showed yellow or brown necrotic zones at pH 3.2 or lower. Field exposure of white pine for 2 months to 2-4 cm of pH 3.2 "rain" per week caused browning of all second year needles. The kidney bean leaves developed necrotic spots (1-2 mm) on 15% to 40% of leaf after as little as three 0.6 cm, pH 3.2 "rain" applications. The soybean and oak developed similar symptoms of equal severity under like treatment. A single (40 minute) application of pH 1.9 to 2.7 "rain" induced random needle injury on the loblolly pine.

(17) Effects of Sulphuric Acid Mist on Plant Canopies

J.B. Wedding, M. Ligotke and F.D. Hess; Environmental Science and Technology, Vol. 7, 1979, pp. 875-878

Particulate emissions from automobiles fitted with catalytic converters consist primarily of sulphuric acid and associated water. The potential impact of such emissions on plants are investigated.

Sulphuric acid solutions (1% and 10% by volume with water) were applied to corn or soybeans by an atomizer in a light (one broad sweeping pass) and a heavy (plants thoroughly inundated) application. Damage was surveyed up to 29 hours after application.

The heavy application of 10% H_2SO_4 resulted in severe damage within 2.5 hours. Foliage was twisted and flaccid and necrotic lesions were forming around the droplets. Lesions did not increase in size suggesting non-translocation of sulphuric acid or neutralization by cytoplasm of cells. The light application

affected younger leaves more than older. Leaves also became flaccid. Chlorotic regions appeared indicating translocation but lesions did not appear.

A heavy application of 1% H_2SO_4 had similar effects as a heavy 10% application except fewer lesions appeared. A light application of 1% H_2SO_4 had no visible effect up to 24 hours later.

A month after the heavy 1% treatment, lesions were still apparent and chlorosis and general senescence was occurring. New tissue was unaffected.

Further experiments involved controlled deposition of fine 1.7 um pure sulphuric acid (18 M) mist over extended periods. Plants did not exhibit damage under this treatment. This may suggest that the threshold for injury was not exceeded, the particles were in a dehydrated state at the low relative humidity, and particles did not contact the plant surface but remained supported on cuticular projections.

Concentrations of H_2SO_4 used in this work are unrealistically high to be applicable to acid precipitation. The initiation of chlorosis is of interest since it does imply translocation of the acid within tissue.

(18) Evaluation of the Effects of Air Pollution on Vegetation in the Mt. Storm, West Virginia-Oakland, Maryland Area

F.A. Wood and S.P. Pennypacker; Paper #75-21.2 presented at 68th Annual Meeting of the Air Pollution Control Association, Boston, Mass., June 15-20, 1975

The occurrence of random dwarfing of pine needles in the Mt. Storm area was investigated as to causal agent. This same problem was investigated independently by Gordon and Tourangeau (1975).

The authors concluded that the agent responsible for the symptoms was biotic after discounting gaseous air pollutants and rainfall acidity. The latter possibility was investigated through application of acid solutions to pine seedlings. This aspect of the study is summarized here.

Candles of Scotch pine were treated with fly ash, sulphuric acid at pH 3.0 spray and sulphuric acid at pH 3.0 and 4.0 spray and eye dropper application. H_2SO_4 and HF were also applied to the pine candles by hypodermic syringe. Two milliliters of 10^{-2} , 10^{-4} , 10^{-5} and 10^{-6} molar acids were applied for 20 successive days.

The fly ash or H_2SO_4 (pH 3.0 and 4.0) did not induce any deleterious effects on the candles. The H_2SO_4 and HF treatments induced necrotic candles or twigs at $10^{-2}M$. At $10^{-3}M$, H_2SO_4 induced necrosis and chlorosis of needles. HF at $10^{-3}M$ induced needle tip necrosis and some short needle development. Less acidic

treatments did not produce any symptoms. HF produced more severe symptoms.

It was concluded that "acid rain" was not responsible for the symptoms observed in the field. The pH 1.7 to 2.7 H_2SO_4 caused necrosis or chlorosis and not the dwarfing of needles. H_2SO_4 at pH 3.7 and higher did not produce symptoms. The acidity required to produce symptoms was greater than the acidity of ambient rain. Symptoms at the needle bases accompanying the short needles induced by HF were not like those occurring in the field. Atmospheric levels of fluorine and fluorine content of foliage were within background levels.

This study effectively contradicts the conclusions of Gordon and Tourangeau (1975). The authors suggest that the causal agent is biotic.

B. TISSUE LEACHING BY ACIDIC PRECIPITATION SIMULANTS

Precipitation leaching of aerial plant tissue is part of the normal cycle of nutrients and other chemical constituents in an ecosystem. Nutrients are thus delivered to understory plants in a forest or to the soil store. Excessive acidity may accelerate this process with undefined consequences.

Efforts to examine the role of excess acid in the leaching solution consist primarily of application of acidic precipitation simulants to plant tissue with subsequent analyses of leachates for nutrient cations. Invariably, such experiments demonstrate accelerated cation losses relatable to acidity of the leaching solution. The net implication for such effects in nature are still unresolved.

(1) Effect of Simulated 'Acid Rain' on Cation Loss from Leaves

J.A.W. Fairfax and N.W. Lepp; Nature, Vol. 225, 1975, pp. 324-325

Rainfall contacting vegetation can leach nutrients from leaves. The role of rainfall acidity in nutrient leaching is investigated for Nicotiana tabacum (tobacco) plants.

Leaching solutions were deionized water (pH 6.7) and dilute H_2SO_4 (pH 3.0). Solutions were applied to plants by misting for 6 hours at 400 ml/hour, collected after interacting with foliage and analyzed for Ca, Mg and K.

Foliar loss of Ca^{++} increased at the low pH, Mg^{++} showed no difference while K^+ loss decreased. A passive ion exchange of Ca^{++} by H^+ is proposed. An explanation for the decrease in K^+ loss is elusive but some possibilities are given. This decrease may be due to the consumption of H^+ ions for the Ca^{++} leaching. Alternately, H^+ may damage the root cell K^+ uptake mechanism.

The loss of Ca^{++} under acid rain regimes may have considerable implications to Ca^{++} cycling if reaction with $SO_4^{=}$ produces insoluble $Ca SO_4$.

The observed decrease in K^+ losses with increasing acidity remain unreconcilable. The reduced K^+ uptake by roots proposal would depend on depletion of Ca^{++} from the roots. The 6 hours of leaching used in these experiments appears to be to short a time for this process to be important.

(2) The Effect of Some Atmospheric Pollutants on the Cation Status of Two Woodland Mosses

J.A.W. Fairfax and N.W. Lepp; In Proc: Kuopio Meeting on Plant Damages Caused by Air Pollution, L.Karenlampi (ed), Kuopio, Finland, 1976, pp. 26-36

Mosses on the forest floor are highly dependant for nutrients leached from the canopy by precipitation. They are effective in sorbing cations in a freely exchangeable form and thus comprise an important reservoir of nutrients in the forest ecosystem. Pollutant gases or acid rain may alter cation uptake and retention characteristics of mosses. While the canopy may reduce H^+ ion concentrations in throughfall, washoff of impacted gases may increase acidity. The role of oxidant air pollution and acid rain in cation relationships in mosses is examined.

The mosses Hypnum cupressiforme and Dicranum scoparium were collected from woodlands in areas subjected to different degrees of air pollution. Treatments consisted of immersion of moss in deionized water (pH 6.8) or H_2SO_4 (pH 4.0) and fumigation with NO_2 followed by water or H_2SO_4 immersion.

Losses of cations from the mosses depended on species, site of collection, exposure to NO_2 and acidity of leaching solution. No overall clear relationship between the variables is apparent. However some patterns do emerge. Simply decreasing pH of the leaching solution results in increased cation losses, except for Mg. Treatment with NO_2 prior to acid leaching increased losses of Ca and Mg.

The increased loss of Ca, K and Na by acid leaching suggest H^+ ions alter the physical - chemical processes binding the cations. A decrease in loss of Mg at pH 4.0 as opposed to pH 6.8 suggests Mg is not freely exchangeable but exists in a complex whose charge is increased by acid treatment and causes tighter binding.

Treatment of Hypnum by NO_2 and acid released more cations than were previously exchangeable. This may be due to a release of tightly bound Mg, breakdown of a Mg complex or destruction of cell membranes (K loss is an indication of membrane damage).

The interaction of air pollutants and cation relationships is very complex. Future investigation of air pollution on nutrient cycles should recognize this complexity.

Nutrient relations are complex and can be altered differently depending on treatment, treatment combinations and condition of the system prior to treatment. In these experiments, there is an attempt to include many variables, some of which no doubt can not be fully defined with a result that data interpretation is difficult and must rely on speculation.

(3) The Effect of Simulated Acid Precipitation on Cation Losses from a Range of Tree Litters

J.A.W. Fairfax and N.W. Lepp; In Proc: Kuopio Meeting on Plant Damage Caused by Air Pollution, L.Karenlampi (ed), Kuopio, Finland, 1976, pp. 123-125

Decomposition of tree litter provides an important source of nutrients for decomposer organisms and is a step in recycling nutrients to the soil and vegetation. Acid rain may affect decomposition rate or enhance cation leaching.

Samples of pure leaf litter from several woody plant species was collected. The surface pH was measured (flat-head electrode) and portions leached for 10 minutes in deionized water (pH 6.8) or dilute H_2SO_4 (pH 4.0). Leachate pH and cation content was measured as were initial cation concentrations (Na, K, Ca, Mg, Zn, Cu) of the litter.

Surface pH of the litter samples were all weakly acid to neutral. The leaching solutions were buffered by the litter. Cations lost by leaching as a percent of total initially present was higher for the pH 4.0 treatments in coniferous litter and, with the exception of Na in Betula, for deciduous litter. Mg loss was substantial in both treatments. Chlorophyll breakdown may account for this release.

Cations released from litter will be retained by complexation with organic matter until subjected to acidic treatments. Accelerated loss of cations from litter may have detrimental effects on decomposers.

These experiments indicate that increasing acidity of rain may accelerate leaching of cations from litter. This would increase rate of nutrient cycling; a short term benefit. Possible alteration of decomposer populations may on the other hand retard nutrient cycling.

(4) A Study of the Effects of Acid Rain on Model Forest Ecosystems

J.J. Lee and D.E. Weber; Paper #76-25.5 presented at 69th Annual Meeting of the Air Pollution Control Association, Portland, Oregon, June 27-July 1, 1976

This paper presents an outline of the experimental design for a project designed to study the effects of acidic precipitation on nutrient cycling.

Forest soil horizons will be reconstructed in lysimeters. Ground flora will be retained and seedlings of sugar maple or alder planted. "Rain" will consist of ionic components determined in Hubbard Brook, New Hampshire rain, acidified with H_2SO_4 to pH of 5.7, 4.0, 3.5 and 3.0. Intensities are 2.5 mm/hour (maple) and 3.3 mm/hour (alder) for 3-4 hours/day, 3 times/week throughout the year.

Sampling and analysis of foliage, litter, soil, throughfall, stemflow, and soil leachate will be used to construct nutrient budgets.

This paper outlines proposed experiments. No results are given. The long term nature of this experiment will make it especially useful in predicting effects of acidic precipitation.

(5) Effects of Sulfuric Acid Rain on Two Model Hardwood Forests

J.J. Lee and D.E. Weber; US EPA Environmental Research Laboratory Report, Corvallis, Oregon, EPA-600/3-80-014, 1980, 39 p.

Lysimeter plots containing a reconstructed soil profile and planted sugar maple or red alder were prepared for treatments with simulated acid rain. The rain simulants were acidified to pH 4.0, 3.5 or 3.0 with H_2SO_4 . A control solution was not acidified (pH 5.6). Overhead nozzles applied the solutions at a rate of 2.8 mm/hr (maple) or 3.7 mm/hr (alder) for 3 hours per day, 3 times/week, throughout the year. (Except during freezing winter periods). Throughfall and litter and soil leachates were collected bi-weekly. Observations on the soil leachates are discussed elsewhere in this bibliography.

Chemical analyses of throughfall for pH, $SO_4^=$, Ca^{++} and Mg^{++} showed no alteration by the tree canopy. This can be attributed to the use of very small trees (less than 5 cm dbh) with little foliage surface area.

Litter leachate chemistry showed a neutralization of acid simulant and an increase in sulphate concentration. Ca^{++} and Mg^{++} in litter leachate was highly variable but there was a tendency for higher concentrations of Ca^{++} with increasing $SO_4^=$ concentration in the leachate. Litter will neutralize the rain percolating into the soil. Increased cation leaching would offset losses from the soil at least in the short term.

These experiments are an attempt to view effects of acidic precipitation on a forest ecosystem. The necessity of using small trees in such models make it difficult to extrapolate to natural forest conditons. Progressive neutralization of rain by canopy and litter will greatly reduce acid input to forest soils.

(6) The Role of Acid Rain as a Regulator of Foliar Nutrient Uptake and Loss

N.W. Lepp and J.A.W. Fairfax; In: Microbiology of Aerial Plant Surfaces, C.H. Dickinson and T.F. Preece (eds), Academic Press, London, 1976, pp. 107-118

This chapter reviews the role of precipitation in the cycling of nutrients from

foliage to understory and soil. Rain will leach nutrients from foliage which can be re-absorbed by the foliage or be returned to the soil. An ion-exchange process where H^+ ions in rain are exchanged for nutrient cations in leaves will result in losses from foliage. Young leaves will have low reserves of exchangeable cations and losses will be less than in older leaves. Increasing the H^+ ion concentrations in the rain would affect the quantity of cations lost and the cycling of these nutrients.

Experiments to determine the effect of acid rain on cation loss and uptake in Hypnum cupressiforme (moss) are described. Moss was collected from unpolluted and polluted sites and exchangeable cations measured after extraction by ammonium acetate. Further samples were successively leached with dilute H_2SO_4 (pH 4.0) and deionized water (pH 6.8) and leachates analyzed. Following these treatments, the samples were placed into a solution containing 10 ppm of Na, Ca, K and Mg (pH 5.6) for 10 minutes and reabsorbed cations extracted by ammonium acetate.

The relative proportions of cations present in the two mosses differ. Acid treatment (pH 4.0) leached cations in the same proportion but the samples from unpolluted sites lost more cations. K loss was highly enhanced by the acid treatment. Uptake of Ca for both sites and uptake of K for the polluted site increased after the pH 4.0 treatment. Moss from polluted sites seems to possess adaptations in foliar ion-exchange mechanisms preventing excessive cation loss following exposure to acid rain.

Subtle but significant changes in the nutrient balance may occur in plants subject to acid precipitation at the pH's presently occurring.

(7) Increases in Foliar Leaching Caused by Acidification of an Artificial Mist

T. Wood and F.H. Bormann; *Ambio*, Vol. 4, 1975, pp. 169-171

H^+ ions in rainwater can replace nutrient cations held on binding sites of the leaf cuticle. Organic acids produced within the plant or carbonic acid in the leaching solution are natural sources of H^+ ions, while strong acids H_2SO_4 and HNO_3 now present in precipitation may affect leaching rates.

Phaseolus vulgaris (pinto bean) plants were exposed to a mist (distilled water acidified with H_2SO_4) at pH 5.0, 4.0, 3.3 and 3.0 for one 6 hour period followed by a distilled water rinse. Leachate was collected and analyzed for Na, K, Mg, Ca and pH. Foliar damage was assessed and leached cations expressed per unit area of leaf exposed.

Acer saccharum (sugar maple) seedlings were similarly treated, except a pH 2.3 treatment was added, seedlings were treated 7 times over 14 weeks and leaves

were not rinsed. Cation losses per treatment were averaged. Losses at pH 4.0 were compared to measured losses at the Hubbard Brook Experimental Forest.

Leaching of Ca, K and Mg increases as pH of treatment decreases. Na does not show such differences.

Necrotic spots were observed in maple after the pH 3.0 and 2.3 treatment. In pinto bean, such spots occurred after a single pH 3.0 treatment. Cell damage by H^+ ions is cited as the probable cause of dramatic increases in losses at high acidity. However, at pH 3.3, no necrosis was observed but losses increased suggesting H^+ ion exchange for cations.

Exchange of cations for H^+ ion in the leaching solution was expected to increase pH of the solution. However, the expected changes would be small (undetectable given the measurement technique) and there was great variability in measurement (due to poorly buffered solution and long storage time). Consequently pH changes were not significant.

Comparisons to losses in the forest indicate some similarity, mainly Ca and K are the most abundant ions lost. However, the quantities lost per unit area of leaf surface and increment of precipitation differ substantially. Under field conditions, foliage can be under greater stress (cuticle abrasion) and the natural leachate would include dry impacted aerosol contributions.

Increasing acidity of rainfall may be affecting natural nutrient cycles.

This work points out the difficulties incurred in comparisons of laboratory results to field observations. Field conditions contain a wide range of uncontrollable variables.

C. THROUGHFALL CHEMISTRY - CANOPY INTERACTIONS

Rainfall chemistry can undergo substantial alterations when it interacts with vegetation canopies and plant stems (tree trunks). Numerous studies have been carried out to characterize such changes. Such canopy interactions are especially relevant to acidic precipitation studies since significant changes in chemistry may occur before the precipitation reaches the soil and eventually aquatic ecosystems. For the sake of brevity, this section contains summaries of publications making specific reference to precipitation acidity.

The most common observation in such studies is a neutralization of precipitation acidity by the canopy. The throughfalling rain invariably contains concentrations of other constituents higher than in the incident rain. There is a difficulty in separating the contribution of dry deposited constituents from those leached from the plant tissue.

Occasionally, precipitation pH may decline upon throughfall. This may occur if the site is near a source of acidic, gaseous air pollution such as SO_2 , or if organic acids are leached from the foliage. The latter may be anticipated in coniferous forests.

(1) Impacts of Acid Precipitation on Coniferous Forest Ecosystems

G. Abrahamsen, R. Horntvedt and B. Tveite; Water, Air and Soil Pollution, Vol. 8, 1977, pp.57-73 also SNSF - Project, Research Report No. 2, 1432 Aas-NLH, Norway, 1975, 15 p.

Field plots and lysimeters are being used to assess the impact of simulated acid rain on soil chemistry, soil zoology and soil microbiology, ie. litter decomposition rates. A summary of results from this part of the study is presented elsewhere in this bibliography.

Some aspects of acid precipitation affects on trees is also considered. Much of this research is conducted apart from the soil work using simulated acid rain.

The chemical composition of incident rain, throughfall and stemflow are examined from two sites, in northern and southern Norway. Deposition of chemicals was greater in the south but it is noted that precipitation rate is higher in the north. Throughfall enrichment of Ca , K and $\text{SO}_4^{=}$ is greater in the south and trees seem to absorb NO_3^- and NH_4^+ from the incident rain. Throughfall beneath spruce and pine contained more strong acid than beneath birch. In the north, strong acid was negligible.

In incident rain, the sea spray component elements Cl , Na and Mg were

correlated while NH_4^+ , NO_3^- , Ca, $\text{SO}_4^{=}$ and acid comprised a second group of correlated elements. In throughfall, Cl, Na, Mg, NH_4^+ , NO_3^- , Ca, K and $\text{SO}_4^{=}$ were correlated. The lack of correlation of other ions and acid was most consistent beneath birch.

The removal of Cl and Na from tree canopies reflects the distance from the site to the sea coast when data from Germany and Sweden are also considered. Removal of S, K, Mg and Ca is considerably higher in the south and probably reflects greater dry deposition.

The concentrations of strong acid, $\text{SO}_4^{=}$, Cl, Ca and Mg was roughly 2 times higher in stemflow than in throughfall. Bark and epiphytes of birch appear to absorb NO_3^- and NH_4^+ . Birch stemflow was more acid than spruce or pine, the opposite to throughfall.

Conclusive interpretation of results is not offered but it is suggested that much of the throughfall enrichment of Cl, $\text{SO}_4^{=}$, Ca, Na, and H^+ is a result of washing off of dry deposits. H^+ ions might be displacing other cations in tree crowns.

The role of soil acidity on germination and establishment of seeds and seedlings is also examined. Seeds were germinated in soil where pH was adjusted by acid or by liming.

Pine seedling germination and establishment was unaffected by soil pH in the range 4.0 to 4.6. Spruce seed experimentation covered a wider pH range, 3.8 to 5.6. Germination exhibited a broad optimum around pH 4.8. Establishment had a narrow optimum around pH 4.9. About 80% of seedlings were abnormal at pH 3.8. Roots did not penetrate the soil.

Assessments of tree growth were based on records of tree ring analysis. Comparison between regions supposedly receiving different inputs of acid precipitation and comparison within regions but from sites of supposedly different sensitivities are made. Thus, this approach is modelled after that of Jonsson and Sundberg (1972). Tree growth since 1927 was examined while the year 1950 was taken as the time when acid precipitation became prevalent. The lack of correlation of tree growth with the acid precipitation effect hypothesis was thought to be masked by environmental variables which could not be adequately defined.

The data presented in this report represent early efforts of the SNSF project. Further efforts are required to elucidate the role of acid precipitation in crown leaching apart from wash off of dry deposition. Seedling establishment can be inhibited by acid soils and soil acidification may induce changes in forest population structure. Tree ring analysis appears too insensitive to assess growth effects induced by acid precipitation, especially where variable sites are used in

the comparisons.

(2) Effect of Atmospheric Sulphur Dioxide on the pH of Rain Intercepted by Forest Trees

J. Baker, D. Hocking and M. Nyborg; In Proc: Workshop on Sulphur Gas Research in Alberta, Information Report NOR-X-72, Environment Canada, Canadian Forestry Service, 1973, pp. 98-102

A gas processing plant emits SO_2 into an area of lodgepole pine dominated forest. The influence of a forest intercepting SO_2 and acidifying rain is investigated.

Weekly samples of incident rain, throughfall and stemflow were collected and analyzed for pH and $\text{SO}_4^{=}$.

At sites near the gas plant, rain pH averaged 5.6 while throughfall and stemflow averages were 5.0 and 4.1 respectively. $\text{SO}_4^{=}$ was consistently higher in intercepted rain.

SO_2 absorbed by needles and tree bark is dissolved in rainwater and throughfall is acidified.

This study demonstrates the role of local sources of SO_2 acidifying throughfall in forests. Alkaline particulates do not appear to play a role here. This is a contrast to areas with high particulate loads where pH of throughfall increases.

(3) Acidity of Open and Intercepted Precipitation in Forests and Effects on Forest Soils in Alberta, Canada

J. Baker, D. Hocking and M. Nyborg; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 449-480

Local sources of SO_2 in the form of natural gas processing plants occur in forested regions of Alberta. In conjunction with soil studies, precipitation and throughfall were collected weekly or after major rain events. The soil study is reviewed elsewhere in this bibliography.

Consistently lower pH was encountered in throughfall, as compared to open precipitation. Stemflow was even more acidic. Increase or decrease in precipitation pH was accompanied by respective increase or decrease in throughfall pH. Stemflow pH did not follow this type of relationship. It is suggest that the acid nature of bark is more important in regulating pH than SO_2 adsorbed onto the bark.

A general trend for increasing pH of precipitation and throughfall through the summer suggests that with frequent summer rain there is reduced potential for SO_2 accumulation in the atmosphere or on foliage.

The data presented in this paper indicates that throughfall near SO_2 sources will contribute to acidification of soil. Data presented but not discussed shows that at a control site, throughfall pH is greater than that of unintercepted rain.

(4) Distribution and Chemical Enrichment of Precipitation in a Southern Norway Forest Stand (July-December 1972)

K. Bjor, R. Horntvedt and E. Joranger; SNSF-Project, Research Report No. 1, 1432 Asa-NLH, Norway, 1974, 28 p. (in Norwegian with English Summary)

Rainfall was collected in open terrain, between trees, and beneath middle of and outer periphery of tree canopies. Throughfall volume at inner and outer positions under spruce was 35 and 99%, under pine, 82 and 83% and under birch 92 and 71% of the incident rain volume in the open. In two between tree collectors the rain volume was 83 and 90% of the open terrain collection.

The deposition of strong acid, Na, Mg and $\text{SO}_4^{=}$ was also monitored. Deposition of strong acid was up to 3 times higher under pine as compared to open terrain. Under spruce acid deposition was about 1.5 times as high, while under birch it was lower than in the open. Sulphate showed similar relationships.

The pH of throughfall ranges from 3.35 to 7.00 while in the open the range was 3.85 to 5.80. Concentrations of Na, Mg and $\text{SO}_4^{=}$ were higher in throughfall. Concentrations were also higher during light rainfalls. Correlations between measured parameters depend on position of collectors. High degree of correlation between Mg and $\text{SO}_4^{=}$ suggests a leaching of Mg from foliage by acid.

On the first day following a dry period the enrichment of sulphate in throughfall correlated with concentrations of sulphate in the air during the dry period.

Enrichments in throughfall by precipitation event are presented. Throughfall under spruce and pine are generally enriched in strong acid, Mg, Na and $\text{SO}_4^{=}$ while under birch there is less enrichment compared to unintercepted precipitation or a consumption (neutralization) of strong acid by the canopy. Under birch, Mg enrichment was especially high just prior to leaf fall.

Since this paper is in Norwegian much of the above observations were taken from figures and tables in the text. The English summary does not contain much discussion. The conifers appear to alter incoming precipitation to a greater extent, including a strong acid contribution to throughfall. Birch on the other hand appears

to neutralize acid in precipitation.

(5) Atmospheric Sulfate Additions and Cation Leaching in a Douglas Fir Ecosystem

D.W. Cole and D.W. Johnson; Water Resources Research, Vol. 13, 1977, pp. 313-317

Acid rain can affect ion leaching and translocation in a forest ecosystem. Studies assessing the role of acid rain in affecting such processes in a Douglas Fir ecosystem in Washington were initiated since sources of acid rain exist in urban areas.

Incoming precipitation and throughfall were examined as well as were soil leachates. Observations relating to soil are reviewed elsewhere in this bibliography.

Incoming precipitation pH frequently fell below 4 but increased upon throughfall. Specific conductance data during rain events suggested canopy leaching during the early part of the storm. During this storm conductance of throughfall and precipitation merged in time, but pH of throughfall remained about a unit higher throughout the event. This suggested hydrogen-cation exchange within the canopy. Foliar sulphate leaching is also suggested.

During a light drizzle pH of precipitation fell below pH 3 but throughfall remained above pH 5. H^+ ion exchange within the canopy reduces H^+ input to the forest floor but appears to accelerate foliar leaching.

An alternative (not discussed by authors) to the observed high conductance of throughfall during the initial period of a storm may have been due to wash-off of dry deposited materials. Throughfall conductance remained high during a light drizzle suggesting that a light rain is more effective in leaching foliage on a per unit volume of precipitation basis.

(6) Solution Chemistry of a New Hampshire Subalpine Ecosystem: A Biogeochemical Analysis

C.S. Cronan; Oikos, Vol. 34, 1980, pp. 272 - 281

The flux of various ions in solution are characterized for a Balsam fir dominated ecosystem in New Hampshire. Solution samples were collected at 5 levels; bulk precipitation, canopy throughfall, forest floor percolate, mineral soil percolate and spring seeps. The data on chemical composition of the solutions collected within the ecosystem were pooled to provide mean and median

concentrations over two growing seasons. The observations noted regarding solution chemistry alterations upon canopy interaction will be summarized here. Soil interactions are considered elsewhere in this bibliography.

The solution chemistry of this ecosystem is dominated by H^+ and $SO_4^{=}$ ions. The pH of incident precipitation was practically unchanged upon canopy interaction. Incident pH was 4.08 and throughfall, 4.02. However, other ions did exhibit concentration changes, mainly increasing concentrations. The possible mechanisms responsible for the increased concentrations of cations and sulphate in throughfall are cited. These are; diffusion of solutes from free spaces in tissue due to high osmotic potential of rain, H^+ ion exchange for foliar cations and wash off of intercepted aerosols and plant exudates. It was felt that the observed enrichment is derived mainly from dry deposition and foliar exudate wash off.

Special attention is given to the throughfall enrichment of K^+ and Ca^{++} with subsequent decrease upon interaction with the forest floor. Ion exchange and/or biological uptake may explain this decrease. NH_4^+ is the other ion apparently subject to biological modification. Concentrations continually decline through the ecosystem components.

Increased throughfall concentration of $SO_4^{=}$ and Cl^- reflect aerosol deposition. NO_3^- decline through the ecosystem is a reflection of the biological demand for this ion.

The anion deficit observed in solutions is probably a result of canopy derived organic anions which were not quantified.

The exchanges occurring between the incident precipitation and the canopy are summarized. Throughfall is enriched in Ca^{++} , Mg^{++} , K^+ , $SO_4^{=}$ and Cl^- and depleted in NH_4^+ and NO_3^- .

(7) Throughfall and Stemflow Chemistry in a Northern Hardwood Forest

J.S. Eaton, G.E. Likens, F.H. Bormann; Journal of Ecology, Vol. 61, 1973, pp. 495-508

The role of precipitation in the removal of nutrients from a forest canopy are examined. This removal contributes to the nutrient flux in forest ecosystems and is dependent on a variety of factors, notably tree species, rain intensity and chemistry, foliage age and chemical composition of the foliage.

Collection and analysis of throughfall and stemflow beneath the canopy at the Hubbard Brook forest, and comparisons to unintercepted precipitation permitted estimation of losses from canopy by precipitation.

It was found that nutrients associated with organic molecules (eg P and N)

moved more slowly to the forest floor upon losses from foliage. Ionic form nutrients (eg. K) moved more rapidly.

The role of H^+ ions in leaching by cation exchange is also considered. The pH of incident precipitation during the study period had a weighted mean pH of 4.06 while the pH of throughfall was 5.01. 91% of H^+ ions remain in the canopy. 27% of the leaching of cations from the canopy can be accounted for by hydrogen exchange in rain.

This additional leaching by acid rain may be one of the effects on terrestrial ecosystems and deserves further study.

This paper contributes to the Hubbard Brook study of nutrient cycling in a forest ecosystem. Acid rain accelerates nutrient leaching and recycling. The question that arises from observations in this study is to the ultimate fate of the excess H^+ ions that remain in the canopy.

(8) Precipitation Acidity: The Role of the Forest Canopy in Acid Exchange

W.A. Hoffman Jr., S.E. Lindberg and R.R. Turner; Journal of Environmental Quality, Vol. 9, 1980, pp. 95-100

The interaction of rain and foliage is examined with specific emphasis placed on the role of strong and weak acids in the aqueous chemistry of a deciduous forest watershed.

Rain samples above and below a canopy of Quercus prinus (chestnut oak) in Tennessee were collected by event and pH, conductivity, sulphate, nitrate, D.O.C. (dissolved organic carbon) and acidity were determined. Organic compounds were also extracted and determined. Contributions of strong and weak acids to total acid are differentiated.

Total acid concentrations above and below the canopy were similar but the ratio of strong to weak acids was altered as precipitation passed through the foliage. During leafless periods the ratio remained unchanged. Sulphuric acid was the main strong acid. The strong acid content of incident rain was inversely related to quantity and intensity of the precipitation while weak acid concentrations decline with increasing quantity but are highest during medium intensity events (1.5 to 5.0 cm/day). Sequential samples (0.25 cm increments) indicated that both strong and weak acids decreased during the course of the event.

The deciduous canopy reduced strong acid concentration by 20 to 40% while increasing weak acid concentration by a comparable amount. Thus total acid is conserved in throughfall. It is suspected that the weak acids are organic in nature but could not account for the total weak acid component. The nature of much of

the weak acid component remains unknown, but probably consists of weak organic and inorganic acids.

Throughfall pH was higher than incident pH during the foliated period but was less or equal during dormant periods. Leaves absorb or neutralize strong acid continually. One might expect exchange site to become saturated if a simple exchange mechanism predominates. Ion cycling and soil neutralization are suggested as sources of neutralizing agents. Leaf surface attrition may also be involved.

Long chain hydroxy carboxylic acids are a possible source for cation exchange and weak organic acids.

Occassional reversals in the pH relationships of throughfall and incident precipitation were observed during foliated periods. Such events followed increased photooxidant concentrations. O_3 reaction with free carboxyl groups will alter the H^+ exchange capabilities.

Lower throughfall pH during leafless periods may be accounted for by rain water displacing sulphates and sulphuric acid from the bark.

The observations noted in this paper are pertinent to an understanding of the interaction of acidity in rainfall with vegetation surfaces.

(9) Seasonal Patterns in Acidity of Precipitation and their Implication for Forest Stream Ecosystems

J.W. Hornbeck, G.E. Likens, J.S. Eaton; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 355-365

A comparison of precipitation acidity for 9 stations in the northeastern United States shows that in the summer, precipitation has a higher H^+ ion concentration. The sulphate component shows similar patterns.

This higher acidity during the growing season means biologic impacts will be at a maximum. One concern should address leaching of nutrients from foliage and soils.

A study of the importance of H^+ ion in foliage cation exchange is examined (see Eaton et al 1973 for more details). This study found that 90% of H^+ ions were lost in throughfall. 27% of the cation leaching from foliage could be accounted for by H^+ ion exchange.

This exchange will reduce the effects of acid on forest soils as well as increase nutrient input to soil. However, the significance of nutrient loss from the canopy and role of H^+ ions remaining in foliage should be considered in assessing net impact to the ecosystem.

During the defoliated condition of winter, H^+ ion input will not be ameliorated by foliage, but snowpack acidity may be lowered by neutralization by organic material such as leaves, bark, fragments, stumps, seed scales, etc. which accumulate in the snowpack. K^+ seems to be an important ion for H^+ exchange in snowpack.

This paper considers the role of forest canopy in altering acidity of precipitation to soil and to streams using data published elsewhere and integrated in this work. Some interactions of precipitation acidity with soil, and resultant inputs to streams are considered elsewhere in this bibliography.

(10a) Leaching of Chemical Elements from Spruce Crowns by Acidified Irrigation Water

R. Horntvedt; Paper presented at: Workshop Meeting to Consider Methods Involved in Studies of Acid Precipitation to Forest Ecosystems, Edinburgh, U.K., Sept. 19-23, 1977 also SNSF-Project, Scientific Paper Reprint No. 20, 1432 Aas-NLH, Norway, 1977, 10 p.

(10b) Leaching of Chemical Substances from Tree Crowns by Artificial Acid Rain
R. Horntvedt; In Proc: IUFRO Meeting, Ljubljana, Yugoslavia, Sept. 18-23, 1978 also SNSF-Project, Scientific Paper Reprint No. 33, 1432 Aas-NLH, Norway, 1978, 10 p.

Leaching of tree crowns by precipitation consists of removal of material dry deposited from the atmosphere, removal of evaporites due to foliage transpiration and leaching from the interior of the plant. Increasing acidity of precipitation may increase leaching of cations from tree canopies.

Preliminary results of the experiments were given by Abrahamsen et al in F.H.Bracke, ed (1976).

Throughfall was collected in a planted Norway spruce stand where acidified ground water was applied by an overhead irrigation system. Treatments consisted of ground water which was acidified with H_2SO_4 to pH 2.5, 3.4 and 6 and applied monthly at a rate of 50 mm over a 3 hour period from May to October. Of the 50 mm of "rain" applied only 30-40 mm was collected beneath the trees. Foliage for chemical analysis was also taken.

In a second experiment, natural throughfall was collected in a mature pine forest where the artificial acid rain was applied to soil beneath the canopy. This was to assess the effect of acid treatments of soil on natural throughfall chemistry. Needles were also taken for analysis.

Throughfall water from the overhead irrigation with acidified or unacidified groundwater was often enriched in K, Ca and Mg and organic carbon. NH_4^+ concentrations were unchanged while NO_3^- declined. Increasing acidity of the treatment increased concentrations of K, Ca, Mg, Fe and Al but not of Na or Cl. The pH of acidified irrigation water did not change upon throughfall but the control (unacidified) water pH decreased from 6.6 to 5.6.

The throughfall collected in June and September was higher in some compounds. It is suggested that partial cutinization or needle senescence is responsible for enhanced losses. Since no visible injury was apparent, the increased leaching at low pH is due to ion exchange from cation pools on the needle surface and not through physiological disturbance.

Some natural throughfall collected after the artificial treatments had variations in sulphur concentrations consistent with the treatments. Sulphate which remained on the foliage was washed off by the natural rain.

The needle analysis did not indicate a treatment effect on nutrient status except for S which was higher from the higher acidity treatments. Trees are able to replace the lost nutrients.

The acid treatment of soil in the mature pine forest did not affect the natural throughfall chemistry.

The results of these experiments demonstrate that leaching of tree canopies by acid rain in effect delivers readily available nutrients to the soil. Uptake from the soil then can easily replace the lost nutrients. If soil nutrients become depleted then a deficiency in foliage may result. These experiments have not differentiated the contribution of dry deposited material or surface evaporites from internal leaching.

Furthermore, the use of groundwater for leaching experiments makes it difficult to access subtle changes in throughfall chemistry.

(11) Assessing the Contribution of Crown Leaching to the Element Content of Rain Water beneath Trees

K.H. Lakhani and H.G. Miller; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 161-172

Rain water passing over tree surfaces shows a gain in element concentrations. This gain is due partly to wash-off of material deposited/absorbed during the dry period and partly to leaching from the foliage. The first component represents an input to the system while the second represents recycling within the

system. It is desirable to distinguish between the sources of elements in throughfall.

The method proposed utilizes collection of incident rain by a standard gauge, a gauge with a wind filter and a gauge collecting throughfall. It is assumed that there is a proportionality between the catching efficiency of the filter gauge and the forest canopy and between the open gauge and filter gauge. A mathematical model is developed that will estimate the contribution to throughfall by foliar leaching.

This approach is applied to data collected for Na and K in a Sitka spruce forest and estimates of leaching losses of Na and K given.

One approach to examining effects of acidic precipitation on forests is to determine the effect of the acidity in foliage leaching. Separation of material washed off the foliage from that which is leached is therefore highly desirable. It is however doubtful if this method could be applied since subtle changes in acid precipitation induced leaching would be undetectable against the large error terms that were produced in application of the model. Furthermore the maintenance of proportionality between collectors could not be guaranteed within the varying physical characteristics of precipitation events.

(12) Acidity of Precipitation as Influenced by the Filtering of Atmospheric Sulphur and Nitrogen Compounds - Its Role in the Element Balance and Effects on Soil

R. Mayer and B. Ulrich; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 409-416

Element fluxes and stores were measured in a birch forest in central Germany. Deposition (wet and dry) was measured beneath the canopy and outside the canopy. Stemflow and litterfall were collected. Water seepage below the humus layer and below the rooting zone was collected. Elemental analyses of plants and soils were conducted.

Input to the soil of most elements is greater under the canopy than outside and may be due to leaching of metabolites or wash-off of material intercepted by the canopy from the atmosphere. This latter, canopy filtered component must be considered an input to the system. To assess this input the relative magnitude of leaching and canopy filtering is measured indirectly.

This measurement is based on the assumption that turnover of elements does not contribute to the precipitation below the canopy during the leafless winter period. The difference between input outside and beneath the defoliated canopy will be the tree filtered component (during the winter). Since such a comparison is

not possible for the summer, an estimate of summer canopy filtering is achieved by applying the ratio attained for the area input by filtering during the winter to the summer. This procedure assumes equal filtering efficiency of foliated and defoliated trees. The annual input of elements by canopy filtering is given.

The input by filtering and wet and dry deposition minus the output below the root zone and the storage in trees gives annual changes in stores in the soil.

It was assumed that $\text{SO}_4^{=}$ and NO_3^{-} in precipitation occurred as acids. More than half of these acids were neutralized by other air contaminants. S and N filtered from the atmosphere and washed out by rain contributed to acidity but are also neutralized to a great extent. The H^+ input to the mineral soil is buffered by Al which forms the buffering system in these acid soils. More than 80% of the acidity is neutralized in the top 2 cm of mineral soil.

The buffering of protons is balanced by loss of Al, Mn, Na, K, Ca and Mg through weathering of silicates and desorption from the exchangeable fraction. The change in chemical conditions in the top 2 cm of soil will affect, for example germination. P uptake and transport can be blocked by Al, Fe or Mn. Losses of Mg may cause this nutrient element to be limiting.

After dividing element flux to soil between atmospheric deposition and recycling from foliage, it was found that H^+ ion was increasing in soil. These already acid soils could still be affected by incoming acid in this relatively unpolluted area.

(13) Input to Soil, Especially the Influence of Vegetation in Intercepting and Modifying Inputs - A Review

R. Mayer and B. Ulrich; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 173-182

A canopy can modify precipitation inputs to the soil by washing off material dry deposited from the atmosphere or by a process of leaching substances previously taken up by roots and translocated to the canopy. To assess the effect of acid precipitation or air pollution on soil it is necessary to know the contribution of leaching to soil input.

Use of collection gauges does not simulate the collection efficiency of a canopy. The ecosystem budget approach must calculate dry deposition by difference between large fluxes and the storage capacity of the ecosystem components are difficult to assess. Measurements of deposition velocity apply only to specific experimental conditions.

In the proposed approach the total atmospheric input to a canopy is measured by a simple collection device near the soil surface. Rain water will remove dry deposition material from the canopy. The necessary assumptions include no dry deposition directly to soil, assimilation and storage of dry deposited material by the canopy is negligible and leaching from foliage is negligible.

Thus the difference in flux above and below the canopy represents dry deposition to the canopy. The assumptions are verified by no observed increase for sulphur in percolating water except for litter decomposition source, low flux to soil of sulphur in litterfall compared to the flux in precipitation and lack of foliar leaching, except for K or Mn observed by comparing growing and dormant seasons.

Data representing dry deposition to beech and spruce canopies is presented using the above assumptions. For aerosols the filtering by spruce is 150% of that of beech. For H^+ and $SO_4^{=}$ the filtering effectiveness of spruce is higher and SO_2 absorption during winter is suggested.

This paper evaluates the role of a canopy in filtering the atmosphere. This effect would be underestimated by wet/dry deposition above the canopy, but would be reflected in throughfall enrichments. The assumption of no interchange between foliage and precipitation during passage through the canopy weakens this proposal for estimation of canopy filtering.

(14) Precipitation and Throughfall Chemistry in the San Francisco Bay Area
J.G. McColl and D.S. Bush; Journal of Environmental Quality, Vol. 7, 1978, pp. 352-357

The chemistry of bulk precipitation and throughfall is determined. Industrial and automobile emissions are suspected of introducing $SO_4^{=}$ and NO_3^- to the precipitation. Although $SO_4^{=}$ was the dominant anion in the precipitation, the best correlation with H^+ was shown by NO_3^- .

Throughfall precipitation (Eucalyptus forest) was enriched in ionic components. Enriched levels of $SO_4^{=}$ were attributed to wash-off of impacted particulates. Higher pH of throughfall was the result of exchange of H^+ by base cations on leaf surfaces. Pollutants impacted to leaves and subsequently washed off during rain events contribute to terrestrial inputs.

In this industrialized area, particulate deposition to foliage neutralizes rain acidity and contributes to ion flux to the soil. Deposition of SO_2 and NO_x in the absence of basic particulates may contribute to throughfall acidity.

(15) Precipitation, its Chemical Composition and Effect on Soil Water in a Beech and a Spruce Forest in South Sweden

B. Nihlgard; Oikos, Vol. 21, 1970, pp. 208-217

The chemical and quantitative differences between incident and throughfall and stemflow rainwater was compared for a beech and a planted spruce forest, in close proximity (50m), in southern Sweden. A greater proportion of incident rain was interpreted by the spruce forest and resulted in a drier soil condition.

Of particular interest are the chemical measurements of the collected solutions. Nutrient cation and anion flux to the soil increases after interaction with the canopy. The flux of K and Mn is especially enhanced while relatively little change is observed for nitrogen. Sulphur and phosphorous flux is enhanced more in the spruce forest. This is attributed to leaching of old, dead and dying needles still on the trees.

pH measurements of various components of the rainwater reveal some significant differences. The mean pH of incident rainwater was 5.2. Beech throughfall and stemflow mean pH's were 5.7 and 4.8 respectively. Spruce throughfall and stemflow pH's were 4.5 and 3.1 respectively. The significance of these observations are not discussed, however it is apparent that beech (deciduous) canopy can decrease the acidity of rainwater reaching the forest soil, while spruce (coniferous) canopy increases this acidity. Leaching of acid organic compounds from spruce along with the low base status of spruce foliage are cited as explanations for the observations.

An experiment using a plastic net to simulate aerosol adherence capacity of foliage was set up to elucidate between aerosol wash-off and foliage leaching as sources of nutrients. Foliage sources of K and Mn in both canopies and of H^+ in spruce are dominant. Mg, Na, Ca and Cl are mainly aerosol derived. Sulphate probably has a leachate source. Nitrogen is precipitated during the rainfall event and not as dry deposition.

This paper does not deal specifically with acid precipitation. However, the observations made have significance in a study of acid precipitation effects. It is noteworthy that the mean pH of incident rainwater was 5.2. The study site is in southern Sweden and the time 1967 and 1968. The extreme acidity of spruce stemflow (pH 3.1) is notable.

Caution must be exercised in interpreting the data since the collection vessels used could have introduced considerable contamination or chemical changes.

(16) Pine Forest Canopy Throughfall Measurements

A. Richter and L. Granat; Report AC-43, Dept. of Meteorology, University of Stockholm and International Meteorological Institute in Stockholm, 1978, 25 p.

It is well recognized that precipitation chemistry will be altered after interacting with a tree canopy. This report presents data on the comparative chemistry of unintercepted precipitation and that of precipitation after passing through a jack pine canopy. The forest is located about 15 km north of Stockholm and is a thin jack pine stand, approximately 150 years of age.

The funnel and bottle collectors were distributed in the forest in such a manner as to approximate "a statistical areal average of the throughfall". This means that collectors would be placed at various positions under a canopy as well as in a position with no vegetation directly overhead. Collectors outside the forest were also employed. Chemical data were derived from pooled samples within and outside the forest.

The resultant data showed that the concentration and deposition of most elements (Na^+ , K^+ , Ca^{++} , Mg^{++} , Cl^- , NO_3^- , $\text{SO}_4^=$ and H^+) was higher in the forest. NH_4^+ was the notable exception, showing a decrease. The pH of samples outside the forest ranged from 4.2 to 4.4 while in the forest the range was 3.4 to 4.0. It was concluded that this acidity was mainly due to sulphuric acid.

An additional experiment was conducted simultaneously. It consisted of collecting increments of an event. Contrary to expectation of an initial rapid washout of material from the canopy, it was found that material was leached at approximately the same rate throughout the event. A rate determined leaching of materials from the foliage is hypothesized but no mechanism for such a process could be proposed. (Only data for Na^+ , K^+ , $\text{SO}_4^=$ and NH_4^+ are reported for this increment study.)

The results obtained can be contrasted to similar studies in deciduous forests where throughfall pH is usually higher than incident. Since the soil pH in the region is higher than the throughfall, there is potential for decreasing base saturation. Throughfall of H^+ and $\text{SO}_4^=$ were about 3 to 5 times greater in the forest. The source of this excess H^+ are $\text{SO}_4^=$ may be of dry deposition origin or may be from the soil.

This study is notable as it includes a rare attempt to examine changes in throughfall during an event. Considerably more information could have been derived from the data. The discussion is quite brief.

D. EFFECTS ON GROWTH AND PRODUCTIVITY

One of the most frequently cited potential effects of acidic precipitation on terrestrial ecosystems is a reduction in productivity of unmanaged natural ecosystems such as forests. Normal agricultural practice would preclude any demonstrable effects to crop productivity. Research efforts attempting to delineate productivity effects have been along two lines; studies of historic growth patterns in forests or simulation experiments involving a variety of plant species.

The first approach has failed to demonstrate conclusively any deleterious effects to productivity under ambient acidic precipitation regimes. The reasons most frequently cited for this are the natural variability in productivity due to the wide range of environmental variables and the potential for nutrients accompanying acidic precipitation to mask deleterious effects due to the acid.

The second, experimental, approach has shown both negative and positive response to acidic precipitation simulants. If treatment acidity is sufficiently high to damage photosynthetic tissue, productivity may decline. On the other hand, nutrient additions in the simulants may enhance growth where such nutrients are limiting.

It is quite reasonable to suggest that productivity decline due to acidic precipitation will not occur until soils become deficient in plant nutrients.

(1) Field Experiments with Simulated Acid Rain in Forest Ecosystems

G. Abrahamsen, K. Bjor and O. Teigen; SNSF-Project, Research Report No. 4, 1432 Aas - NLH, Norway, 1976, 15 p.

Theoretically, the result of acidic precipitation would be a reduction in plant growth induced through changes in soil characteristics. This paper serves as an introduction to field experiments aimed to elucidate affects of acid precipitation on tree growth, ground cover vegetation and chemical and biological properties of soil.

Preliminary results of one experiment, dealing with soil, are given in Abrahamsen et al (1975).

Five experimental plots in two areas in southern Norway are used. Soil characteristics of the plots are given elsewhere in this bibliography. Vegetation in the plots consists of recently planted stands of pine, spruce and birch or of naturally revegetated Scots pine. Ground cover vegetation is also described.

The treatment consists of watering by ground water acidified with H_2SO_4 . 25 or 50 mm of the "rain" is applied monthly during the frost free period. Non-

irrigated areas are also established. Crushed limestone is applied in some cases. Treatment combinations, replications, plot size, etc. are summarized in a table.

The acidified ground water is applied from over-head pipes and spray equipment or from within the stand in the case of the mature, naturally revegetated Scots pine stand.

The necessity of simplification of experimental procedures limits the applicability of results to naturally occurring acid rain. Nutrient content of ground water is not similar to the nutrient content of precipitation. High rates of acid and $\text{SO}_4^{=}$ application were necessary to compress the time frame for experiments.

Site descriptions and experimental design are presented in this report. No data or results are presented.

(2) Forest Ecosystem Responses to Acid Deposition - Hydrogen Ion Budget and Nitrogen/Tree Growth Model Approaches

F. Andersson, T. Fagerstrom and S.I. Nilsson; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 319-334

The effects of acid precipitation can be assessed by examining H^+ ion budgets. The budgets of 3 forests in Europe and the USA are compared. A nitrogen dependent tree growth model is discussed. These two approaches may be used to assess effect of acid deposition to whole ecosystems.

The flow of H^+ ions in a forest ecosystem can be derived from flows of other ions. The 3 forests under different deposition regimes are compared in terms of importance of deposition relative to internal processes, capacity to neutralize H^+ ions by mineral weathering and possible losses of H^+ ions from the system.

Hydrological flows of H^+ ions are small compared to biological and chemical flows. $\text{NH}_4^+/\text{NO}_3^-$ balance determines hydrogen ion flow to a large extent; with nitrification acting in an acidifying direction.

With a more complete data base for ion balance in ecosystems it may be possible to relate the importance of acid deposition in relation to internal flows of H^+ .

Acid deposition has not been shown to decrease tree growth on a regional scale. Internal buffering or input of counteracting components such as nitrogen may be the reason. Plant growth may be limited by nitrogen but also depends on the acid base status of the soil. A relationship between acid base status and nitrogen content of humus has been demonstrated. Adverse affects will involve nitrogen transformations as well as changes in soil chemical processes.

A mathematical model is used to test the effects of acid deposition on pine forest growth by assuming different parts of the nitrogen cycle are affected. Reduced mineralization of root and needle litter would reduce growth while N deposition would increase growth.

Growth responses to acid deposition are not likely to be detectable since the acid input is small compared to internal flows. Nitrogen cycling effects may be more important.

(3) The Effect of Acid Precipitation on Tree Growth in Eastern North America

C.O. Cogbill; Water, Air and Soil Pollution, Vol. 8, 1977, pp. 89-93

Tree growth as reflected by tree ring analysis was examined to see if acidic precipitation and forest growth histories were correlated. Two sites were selected, both in mountain areas, with acid soils and isolated from local pollution sources. One site was in the centre of the acid precipitation region and one outside the region (NE USA).

Response indices (ratio of yearly growth to previous 10 year average) were used as the dependent variable in a regression analysis against climatic variables. Growth trends could not be accounted for by weather variables.

Examination of radial and basal area increments of trees in the two regions did not establish differences in growth despite differences in acid precipitation regimes. Due to unknown initiation date of acid precipitation and to a large variance of tree growth estimates, a correlation of forest growth and acid precipitation could not be established.

An attempt to establish effects of acid precipitation on tree growth would be very difficult to do in light of the numerous naturally occurring variables which can not be fully documented. Such variables would have an influence greater than the relatively subtle effects of acid precipitation.

(4) The Nature, Distribution and Effects upon Vegetation of Atmospheric Impurities In and Near an Industrial Town

C. Crowther and A.G. Ruston; The Journal of Agricultural Science, Vol. 4, 1911-12, pp. 25-55

Rain samples from the vicinity of the industrial town of Leeds were collected and analyzed for a number of impurities, notably N, S, Cl, tar, ash and free acid. One observation was that rain contained a considerable amount of free acid which

was attributed to the combustion of coal in the area. Ash trees occurring in areas of higher deposition of H_2SO_4 were observed to lose their leaves earlier.

Other impurities in the air would exercise a detrimental influence on vegetation. For example, insoluble suspended impurities would reduce light intensity and block stomatal openings. Nitrogenous components would be beneficial. Obvious detrimental soluble impurities would be the free acid and sulphur compounds SO_2 and H_2S .

Experimentation on the effect of H_2SO_4 acidified water on the growth of Timothy grass was conducted. The grass was sown and watered with dilute H_2SO_4 solutions or rain collected at Leeds or Garforth (six miles from Leeds). The acidities of watering solutions are expressed in units of parts H_2SO_4 per 100,000 (1, 2, 4, 8, 16 and 32 parts). Assuming that the H_2SO_4 was added to distilled water, corresponding pH of these solutions are 3.0, 2.7, 2.4, 2.1, 1.8 and 1.5. Leeds rain acidity ranged from 0.5 to 10 parts (pH 3.3 to 2.0).

Yield decreased with increasing acidity of watering solution. The grasses receiving the heaviest acid application were killed in 6 months. Yield declined progressively over the 3 years of treatment. Nitrogen content decreased while crude fiber content increased. The Leeds rain treatments were showing deleterious effects by the 3rd year.

Subsequent soil analysis suggests that changes induced in the soil is responsible for the observed effects on vegetation. Soil observations for this work are summarized elsewhere in this bibliography.

It is significant that at the time of this investigation, some 70 years ago, it was recognized that impurities in rainwater, notably acid, will have deleterious effects to plants. While treatments were unrealistically severe it is notable that ambient rain from Leeds initiated a negative response in the yield of grass. It should be noted that such industrial areas as Leeds suffered severe pollution in the early part of this century.

(5) Some Effects of Simulated Acid Rain on the Growth of Barley and Radish
 S.A. Harcourt and J.F. Farrar; Environmental Pollution (Series A), Vol. 22, 1980,
 pp. 69-73

The effect of spraying radish and barley plants with solutions of dilute H_2SO_4 (pH 5.5 to 2.5), with and without other ionic constituents found in rain water or sulphite are examined. Productivity of root and leaf systems are the measured parameters.

The application rate of the test solutions was 100 ml per 15 cm diameter pot,

7 times at intervals of 4-5 days. This was equivalent to 4 cm of rain.

Radishes treated with dilute H_2SO_4 showed reduced leaf area and leaf dry weight and reduced fresh and dry weight of roots at pH 2.5 but not at 3.5. Addition of 0.1 mmol dm⁻³ sulphite had a significant interaction with pH. This interaction did not occur if the solution contained the other ionic components of natural rainwater.

The barley experiments did not include the pH 2.5 treatment level and the solutions contained other rainwater components. The addition of sulphite reduced above-ground biomass, with the effect not significantly dependent on pH.

The treatment levels, pH 3.5 and greater are realistic in terms of sulphur deposition when compared to measured deposition in Great Britain. The results suggest a possibility of reduced plant productivity by ambient acid rain.

The differences in plant response to various combinations of pH, sulphite and other rainfall components seen in these experiments, suggest that H_2SO_4 alone is not a useful simulant in simulated acid rain experiments.

(6) Response of Soybeans to Acid Precipitation Alone and in Combination with Sulphur Dioxide

P.M. Irving and J.E. Miller; In: Radiological and Environmental Research Division Annual Report, Argonne National Laboratory, Argonne, Illinois, Jan.-Dec. 1977, ANL-77-65, Part III, pp. 24-27

The effect of acid precipitation administered during the entire life cycle of plants is examined as is the interaction of SO_2 and acid rain.

Soybeans were grown in open air fumigation systems and subjected to acid (pH 3.0) and control (pH 5.6) simulated rain combined with low and high (786 ppb) SO_2 fumigations.

Plants under the acid precipitation treatment had an apparent (not statistically significant) lower seed yield with and without SO_2 . This may be due in part to lower dry weight per seed produced under the acid treatment.

Acid precipitation treated plants had higher photosynthetic rates and lower diffusive resistance. An apparent increase in effect through time suggests a cumulative effect on plant metabolism. Higher chlorophyll content in acid treatments suggests a delay in senescence. Erosion of epicuticular wax appeared higher under acid treatment. A potential for increased transpiration losses and pathogen infection exists.

Physiological processes may be affected through changes in cellular pH affecting enzyme or hormonal activity.

Much of the information presented appears preliminary. Most differences observed between treatments are not statistically significant.

(7) The Effects of Acid Precipitation Alone and in Combination with Sulphur Dioxide on Field Grown Soybeans

P.M. Irving and J.E. Miller; In: Radiological and Environmental Research Division Annual Report, Argonne National Laboratory, Argonne, Illinois, Jan.-Dec. 1978, ANL 78-65, Part III, pp. 17-20

Field grown soybeans were exposed to acid (pH 3.1) or control (pH 5.3) precipitation with and without SO_2 fumigations. "Rain" was applied every 5 to 7 days in July and August with 34 cm applied in 1977 and 45 cm in 1978. SO_2 fumigations (4 hours) averaging 0.79 or 0.19 ppm were performed 24 times in 1977 and 17 times in 1978.

Seed yield was unaffected by acid or control simulants, nor was SO_2 interaction observed. SO_2 fumigated plants had lower yields. 1977 seed yield was slightly lower under acid treatment. In 1978, yield in unfumigated acid treatment plants was somewhat higher. Weights of individual seeds were consistent with yield differences.

Photosynthesis was higher in control and acid treated plants compared to untreated plants. Additional water may be the stimulant. SO_2 reduces photosynthetic rate but acid precipitation modifies this effect. Chlorophyll content was higher in unfumigated acid treated plants while SO_2 reduces chlorophyll content.

Visible damage was not apparent but histological examination revealed significantly greater numbers of dead leaf cells in all plants except those exposed to control precipitation alone.

The proportion of dead mesophyll cells in the combined SO_2 -acid treatment was greater than additive effects of each treatment.

Toxic effects of the two pollutants depends on entry rate and distribution within tissue. Plant growth may be stimulated by nutrients in acid rain or by SO_2 at low concentrations.

An apparent interaction which is not discussed is the contrasting affects of acid precipitation. Higher chlorophyll content of acid treated plants together with nutrient benefits may be counteracted by cell destruction, resulting in no changes in yield.

(8) Polluted Rain and Plant Growth

J.S. Jacobson, J. Troiano, L.J. Colavito, L.I. Heller and D.C. McCune; In: Polluted Rain, T.Y. Toribara, M.W. Miller and P.E. Morrow (eds), Plenum Press, New York, 1980, pp. 291-305.

Nitrate and sulphate in precipitation constitute a source of nutrients for plants. Ozone is phytotoxic. High acidity of rain may cause direct injury to plants, leach essential nutrients from foliage or disrupt physiological functions.

Experiments were conducted to assess the interaction of NO_3^- , $\text{SO}_4^{=}$ and acidity of rain and ozone in the air on growth and yield of plants. In one series of experiments Lactuca sativa (lettuce) grown in a sand culture in a greenhouse was exposed to "rain" at pH 3.2 for a 2 hour period, 3 times at 5 day intervals. Nitrate and sulphate concentrations were varied to give $\text{NO}_3^-:\text{SO}_4^{=}$ ratio of 1:7.5, 2:1 and 30:1. Growth was assessed 24 hours after the last treatment.

In the second series of experiments, field grown Glycine max (soybean) was exposed to simulated acid rain at pH 2.8, 3.4 or 4.0 in paired chambers. 18 one hour applications of 0.5 cm were made over a 2½ month period. Filtering air in some chambers reduced O_3 to less than 0.03 ppm. In unfiltered air, O_3 reached concentration as high as 0.125 ppm. Productivity was assessed at the end of the 2½ month period.

Growth of lettuce, as dry weight, was affected by changes in $\text{NO}_3^-:\text{SO}_4^{=}$ ratios. Apical leaf and root weight was reduced at the highest NO_3^- to $\text{SO}_4^{=}$ ratio compared to lower ratios or at pH 5.7.

The weight of vegetative soybean tissue was reduced in the pH 2.8 and 3.4 treatment as compared to pH 4.0 in high O_3 . Differences were not significant at low O_3 . Bean yield was greater at pH 2.8 and 3.4 and low ozone but no differences were observed at high ozone. While ozone suppressed growth and yield at all acidities, the depression was greatest at pH 2.8. Acidic rain produced a shift of photosynthate from vegetative organs to beans at low ozone but not at high ozone.

The importance of considering conditions of plant nutrition and air pollution during experimentation assessing acid rain affects on plants is emphasized.

The reduced productivity of lettuce at the high $\text{NO}_3^-:\text{SO}_4^{=}$ ratio is not discussed but appears to contradict expectations.

(9a) Soil Acidification by Atmospheric Pollution and Forest Growth

B. Jonsson; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 497-501

(9b) Has the Acidification by Atmospheric Pollution Caused a Growth Reduction in Swedish Forests? A Comparison of Growth Between Regions with Different Soil Properties

B. Jonsson and R. Sundberg; Research Note No. 20, Department of Forest Yield Research, The Royal College of Forestry, Stockholm, Sweden, 1972, 48 p.

It is clear that a general acidification of the environment has been taking place over the past few decades. Soils subjected to H_2SO_4 deposition may become impoverished over the long term. In soils subjected to acidification this results in accelerated impoverishment and may reflect in lower vegetation growth rates as compared to less susceptible soils. The hypothetical difference in growth between regions of different susceptibility to acidification is the object of study in this investigation.

Two types of regions in southern Sweden were categorized on the basis of soil and water chemical characteristics, as regions more susceptible to acidification versus regions less susceptible.

Growth data as derived from tree ring width analysis were compared for the more sensitive and less sensitive sites. Tree ring increments are a result of biological processes and the question of whether deposited S has affected these processes and therefore growth is addressed.

The criteria for region selection are the magnitude of acid fallout and information about pH and ionic composition of lakes and rivers. The main criterion has been based on information regarding distribution of soil types.

Regions with soil of low base status or glaciofluvial sand deposits and surface water of low pH and low cation concentration would be regarded as susceptible to atmospheric chemical influence.

A statistical model to differentiate between annual growth of trees from the two regions was introduced. The growth trends for trees from the two regions were compared from the time when possible effects of acidification were expected to become manifested (ca. 1945/1950). The observed differences in growth trends between the two regions could not be regarded as reflecting statistical certainty in the estimates.

This investigation was designed so that a possible reduction in growth resulting from acidification could be detected. The observed reduction could not be attributed to any cause other than acidification. Acidification cannot be excluded as a possible cause of poorer growth and may be suspected to have had an

unfavourable effect on growth within susceptible regions.

The investigation gives only an impression of the order of magnitude of average annual growth reduction in the period 1951 - 1965 for susceptible relative to less susceptible sites. Values of 0.3 and 0.6 % reduction are proposed but it is pointed out that between 1945-65 productivity of Swedish forests has increased as a result of better forest management.

The summary given above was taken from the abbreviated (1977) version of the original (1972) report by Jonsson and Sundberg. The original contains details of the statistical model used.

Although many naturally occurring variables were considered in this attempt to detect growth reduction, it is extremely difficult to detect small changes among much larger natural fluctuations. It seems doubtful that productivity changes as a result of acidification can be detectable at this time.

(10) Sulphuric Acid Rain Effects on Crop Yields and Foliar Injury

J.J. Lee, G.E. Neely, and S.C. Perrigan; US EPA Environmental Research Laboratory Report, Corvallis, Oregon, EPA - 600/3-80-016, 1980, 20 p.

This study was designed to determine the relative sensitivity of crop plants to simulated acid rain. 35 different cultivars were grown in field chambers and exposed to a simulated rain solution pH 5.6 or with additions of H_2SO_4 (pH 4.0, 3.5 or 3.0). Application rate was 6.7 mm/hr., 1.5 hrs/day, 3 days/wk for a total of 30 mm/wk. Plants were grown in a sandy loam soil with peat moss and fertilizer amendments. Yield (marketable portion weight) and foliage injury were assessed.

A differential response was noted between dicotyledons and monocotyledons. While stimulation of yield was observed for both groups, inhibition occurred only with the dicotyledons. As a group, the dicots showed more sensitivity to foliage injury. Further discussions of crop response were divided on the basis of type of crop, ie. root, leaf, grain, fruit etc.

Of the root crops, beet was injured at pH 4.0, radish at 3.5 and carrot at 3.0. Yield of carrot was most severely depressed, followed by radish and beet. At pH 4.0, carrot yield was 73% of the control while no foliage injury was observed. An interesting observation was made in relation to treatment acidity and pest damage. Pests were less prevalent in high acidity chambers.

The leaf crops, Swiss chard, mustard greens and spinach were sufficiently injured by acid to affect marketability. Lettuce and tobacco were less affected, and cabbage the least sensitive. Yield reduction occurred only in mustard greens.

The cole crops, broccoli and cauliflower were injured at pH 3.0 and 3.5;

cabbage only at 3.0. The waxy foliage provided only partial protection from rain acidity. The only yield reduction occurred with broccoli at pH 3.0.

The only tuber crop, potato, had a mixed response. Injury occurred at pH 3.0 and 3.5. Yield was inhibited at pH 3.0 and stimulated at 3.5 and 4.0.

At pH 3.0, all fruit crops, (tomato, cucumber and green pepper) showed foliar injury. Less injury occurred at pH 3.5 and only the pepper was injured at pH 4.0. Tomato yield was greater under the acid treatments but damage to tomato fruit affected marketability at pH 3.0.

Yield of small grain crops (oats, wheat, barley) was unaffected and no injury was apparent. Corn exhibited some foliage injury.

Onion bulbs tended to be heavier in the acid treated plants. Foliar injury was not observed.

The forage crops (fescue, orchard grass, bluegrass, ryegrass and timothy) were injured at pH 3.0 and 3.5. Slight injury to bluegrass occurred at pH 4.0. Although injured, yield of orchard grass and timothy was enhanced at pH 3.0.

The summary of results indicates that of the 35 cultivars used, 31 were injured at pH 3.0, 28 at pH 3.5 and 5 at pH 4.0. Data on yield and foliar injury was obtained for 28 crops, those grown to maturity. Observations on yield and injury were made on the basis of crop treatment combinations (3 acid treatments x 28 crops = 84 combinations).

Foliar injury occurred in 46 of the 84 combinations; 5 occurring at pH 4.0. Enhanced yield occurred in 7 of those 46 combinations and lower yield in 9 of the 46. This suggests that foliar injury does not necessarily lead to yield reduction.

This study is perhaps the most extensive yet reported on the direct effect of simulated acid precipitation with respect to foliar injury and crop yield. Uniform treatment of a wide variety of crop plants is necessary to delineate differential sensitivities. The results suggest great variability in response, both positive and negative, to acid precipitation. The mechanism(s) for such response must still be resolved.

(11) Effect of Simulated "Acid Rain" on Juvenile Characteristics of Aleppo Pine
(Pinus halepensis Mill.)

D.I. Matziris and G. Nakos; Forest Ecology and Management, Vol. 1, 1978, pp.267-272

The effect of simulated acid rain on growth and other characteristics of Pinus halepensis are examined. Intraspecific variability is also examined as are effects on soil properties.

Seedlings were irrigated with deionized water acidified with H_2SO_4 to pH 3.1 or 3.5. Deionized water was the control. The application was about 100 mm per month for 6 months. Subsequently, height was recorded and needles taken for sulphur determination.

The height of seedlings decreased with increasing acidity of treatment while sulphur content of needles increased. The pH 3.1 treatment suppressed growth by 8.2% over the control. Terminal bud formation decreased and mortality increased with acid treatment.

The growth of seedlings from different families (seeds from different trees) was proportionately suppressed with acid treatment.

Changes in soil properties were observed and summarized elsewhere in this bibliography.

A discussion of the reduction of growth with acid treatment related to changes in soil properties is not given. The effects of acid treatment on growth must be directed through the soil since the treatment was applied by irrigation.

(12) The Optimum Nutrition Experiment Lisselbo. A Brief Description of an Experiment in a Young Stand of Scots Pine (*Pinus silvestris L.*)

C.O. Tamm, A. Nilsson and G. Wiklander; Research Note No. 18, Department of Forest Ecology and Forest Soils, The Royal College of Forestry, Stockholm, Sweden, 1974, 25 p.

The study of effects of nutrient additions, through fertilization, on forest productivity is the main objective of this work. Various combinations of the nutrients, N, P, K, Mg, S and micronutrients were applied to a Scots pine stand in Sweden. In some experiments H_2SO_4 and lime were applied to assess the potential affects of acid precipitation on productivity. Needle nutrient content and height and diameter growth are the parameters being observed.

This report contains a number of figures and tables outlining treatment regimes and also some results but there is no discussion of the data. It appears that there is no discernible effect of the acid on growth or nutrient content of the trees. Since it is believed that effects of acid rain will be directed through the soil, lysimeters are being used to study leaching of nutrients with the various treatments. Changes in soil chemistry (A_0 horizon) are also being followed.

(13) Effects of Application of Sulphuric Acid to Poor Pine Forests

C.O. Tamm, G. Wiklander and B. Popovic; *Water, Air and Soil Pollution*, Vol. 8, 1977, pp. 75-87

This paper summarizes the results of experimentation involving additions of H_2SO_4 and nutrients to forests (Tamm *et al* 1974). Parts of this paper deal with soil and soil microorganisms and are summarized elsewhere in this bibliography.

Forest plots were treated with various combinations of H_2SO_4 , NPK fertilizer, lime, micronutrients and water (irrigation).

Nitrogen is the factor limiting growth at the site. Additions of other nutrients did not improve growth. Stem volume growth can be related to an optimum N concentration in needles. N fertilization increased basal area of trees more than height. Irrigation improved growth if combined with fertilization.

Application of H_2SO_4 at 100 kg/ha/yr killed ground flora of lichens, mosses and shrubs but has had no visible negative effect on tree growth. Measurement of basal area growth differences may be too crude to detect changes.

(14) Effects of Artificial Acid Rain on the Growth and Nutrient Status of Trees

B. Tveite and G. Abrahamsen; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 305-318

Studies of possible growth effects by acid precipitation under natural conditions have been inconclusive. Simulation experiments have produced variable growth responses depending on species, magnitude of acid application and extent of the nutritive value of treatment solutions. Results of acid simulation and liming experiments in Norwegian pine and spruce forest are presented.

Field plots of pine and spruce were watered with ground water acidified with H_2SO_4 to as low as pH 2. Various lime treatments were applied to plots. Watering was at a rate of 25 or 50 mm/month. Five waterings were carried out during the frost free period.

Height and/or girth of trees were monitored. Nutrient status was examined by needle analysis.

Observation of tree growth indicated an increase due to application of "rain" at pH 2, 2.5 and 3 to Scots pine saplings while liming had no effect. The longest experiment involved lodgepole pine. The lowest treatment pH was 3 and no negative growth effects were observed after 5 years.

The nutrient status of current year needles do not depart from optimum

values except for N and possibly S. Scots pine showed an increase in N level in response to acid treatments. Sulphur concentrations increased after treatment with rain of pH 2.5 and 2. Similar observations were made for Norway spruce while lodgepole pine did not respond to acid treatments.

The stimulated growth in Scots pine is attributed to increased N uptake from the soil. The beneficial effect by S fertilization cannot be excluded.

Short-term effects of acid precipitation appear to be increased N and S uptake. The treatments required to produce these observations are not realistic in terms of ambient rain conditions. NO_3^- input in rain may cause short term growth stimulation but the effects of losses of cations through soil acidification is still unknown.

The authors suggest that growth stimulation by the addition of acid is a result of increased N uptake from soil. The observed stimulation is small and not at all consistent. Possible mechanisms for this increased uptake are not discussed.

(15) The Hubbard Brook Ecosystem Study: Forest Biomass and Production
R.H. Whittaker, F.H. Bormann, G.E. Likens and T.G. Siccama; Ecological Monographs, Vol. 44, 1974, pp. 233-252

This paper addresses the measurement of forest biomass and productivity at the Hubbard Brook Experimental Forest. Extensive methodology and data are presented.

A notable observation recorded for productivity as measured by stem wood volume increments is a decline in growth after 1960. The decrease is abrupt and intense. This period was the time of drought but also the time of increasing acidity in rainfall. The history of tree growth in this area can be followed for over 2 centuries and does not record such a decline prior to 1960. Further investigation is suggested.

This reduced rate of productivity should not be readily attributed to pollution by acid rain. Drought was suggested as an alternative. If the forest is approaching a climax state, net productivity will decline.

(16) The Effects of an Artificial Acid Mist upon the Growth of Betula alleghaniensis Britt.

T. Wood and F.H. Bormann; Environmental Pollution, Vol. 7, 1974, pp. 259-268

Increasing acidity of precipitation may affect vigour and growth of forest

trees. Response of Betula alleghaniensis (yellow birch) is examined under experimental conditions.

Seedlings were established in a loam soil and subjected to misting with H_2SO_4 acidified distilled water at pH 4.7, 4.0, 3.3 3.0 and 2.3. Misting was conducted for a 6 hour period weekly, 11 weeks for 6 week old seedlings and 15 weeks for 2 week old seedlings. Mist intensity equalled 0.5 cm of rain/week.

Throughout the experimental period, seedlings were harvested from a surplus group and growth parameters measured.

Symptoms of damage at high acidity treatments consisted of necrotic spotting of 0.5 mm diameter at pH 3.0 to over 5 mm at pH 2.3. Abnormal leaf morphogenesis (curling and shortening of blades), death of individual leaves and entire plants was observed at these high acidity treatments. Changes in soil pH and exchangeable bases were assessed.

Differences in growth (plant weight, total leaf area, stem length) were not significantly different in either 6 or 2 week seedlings exposed to mist at pH 4.7 to 3.0. At pH 2.3, growth was reduced. Symptoms implying photosynthetic tissue destruction were noted at pH 3.0. Growth measurement techniques were not sensitive to detect probable growth reduction at the pH 3.0 level but there are implications for growth reduction over longer periods of time.

Impaired leaf development at pH 2.3 (6 week seedlings) produced a 40% reduction in leaf area and 25% reduction in leaf weight. Death of almost all "2 week seedlings" and survival of all "6 week seedlings" at the pH 2.3 treatments suggests that seedlings in the cotyledon stage are especially sensitive to acid rain.

While growth may also be affected by changes in soil chemistry, the observed changes in exchangeable bases cannot be properly assessed due to the use of tap water for irrigation.

A possible implication from this work is that the threshold for growth reduction lies between pH 3.0 and 2.3 and requires repeated treatment with acid. Whether forest productivity can be reduced through foliage effects if rainfall is consistently at pH 3.0 cannot yet be ascertained.

(17) Short-term Effects of a Simulated Acid Rain upon the Growth and Nutrient Relations of Pinus strobus, L.

T. Wood and F.H. Bormann; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 479-488

The growth and nutrient relations of Pinus strobus (white pine) subjected to simulated acid rain are examined. Changes in soil chemistry are also examined as nutrient flows and budgets are constructed in these artificial ecosystems.

Detailed observations of soil effects are reviewed elsewhere in this bibliography.

Pine seedlings, germinated in a loam soil, were subjected a weekly 6 hour application (12.5 cm) of "rain" for 20 weeks. Rain was distilled water acidified to pH 5.6, 4.0, 3.3, 3.0 and 2.3 with H_2SO_4 , HNO_3 and Cl in anion proportions of 66, 20 and 10% respectively. Leachate from soil was collected and analyzed for K, Mg, Ca and pH.

After the 20 week treatment seedlings were examined for damage and growth parameters measured. Nutrient content of needles, stem and roots was determined (K, Mg, Ca and N). Soil exchangeable cations (K, Mg, Ca) and N was determined and nutrient budgets constructed.

Growth of seedlings was stimulated at the pH 2.3 treatment level. Increased N assimilation suggests fertilization by the NO_3^- in the rain. This growth increase occurred despite the incidence of tissue damage and necrotic needle segments on all seedlings treated by pH 2.3 rain. In the long run, tissue damage may reduce productivity.

Assimilation of K, Mg and Ca was fairly random within treatments of pH 3.0 and 5.6. At pH 2.3 cation assimilation was lower in spite of increased growth and attributed to lowered availability from soil or leaching losses from foliage.

It is apparent that, in the short term, inputs of NO_3^- will stimulate growth if nutrient cations do not become limiting. If soil losses continue, productivity will be reduced.

Such a reconstructed ecosystem approach is useful for assessing the impact of acidic precipitation on vegetation as it at least approximates natural conditions. Longer term experiments of this type would likely contribute more definitive information.

E. EFFECTS ON PLANT REPRODUCTION

Deleterious effects on plant reproduction may occur where toxic components of precipitation such as H^+ or other ions interact with sensitive plant organs. If spermatazoid activity or pollen tube elongation are inhibited, reproduction may be reduced with subsequent loss of ecosystem stability. The limited research in this area has been conducted under experimental laboratory conditions.

(1) A Plant Developmental System to Measure the Impact of Pollutants in Rain Water

L.S. Evans; Journal of the Air Pollution Control Association, Vol. 29, 1979, pp. 1145-1148

Previous work (Evans and Bozzone 1977, 1978) is discussed here. Buffered solutions used to assess sperm mobility in bracken fern and previously reported to be at pH 5.8, 5.6, 5.2, 4.8, 4.2, 3.2 and 2.2 are corrected to read 6.1, 6.0, 5.5, 5.1, 4.5, 3.6 and 3.0.

After a 2-4 minute exposure to sulphate at 43.3, 86.6 and 173.2 μM , sperm motility decreased 35-42%, 47-62% and 60-70% at the respective sulphate concentrations and at all pH levels.

During the 3.5 hour course of the fertilization experiments, the pH of the buffers, added to vermiculite, also changed. The acid became less so and the higher pH buffers became more acidic. This change was not previously mentioned.

Exposure to sulphate at 43.3, 86.6 and 173.2 μM reduced fertilization by 13, 26 and 38% at all pH levels. Fertilization at pH 5.6, 5.1 and 4.5 was reduced by 8, 24 and 35% when compared to pH 6.2 at all sulphate concentrations.

Effects of Cl^- , NO_3^- and $SO_4^{=}$ were similar. Effect of two anions in combination was similar to the effect of twice the concentration of one anion.

The use of biological systems is discussed as a mechanism for assaying effects of toxic substances in the environment.

This paper summarizes work previously presented. The reported change of buffer pH when applied to the vermiculite points to the importance of soil conditions affecting pH and anion concentrations of the impacting rainfall.

(2) Effect of Buffered Solutions and Sulfate on Vegetative and Sexual Development in Gametophytes of Pteridium aquilinum

L.S. Evans and D.M. Bozzone; American Journal of Botany, Vol. 64, 1977, pp. 897-902

Genetic recombinations in ferns occur when motile sperm are able to reach the archegonia. A moisture film is required to permit fertilization. The acidity of this water may be affected by acidic precipitation. Sperm motility and fertilization success is assessed in relation to pH and sulphate concentration.

Spermatazoids were introduced into solutions buffered by a citrate-phosphate buffer to a pH ranging from 2.2 to 5.8. Sperm motility was recorded at timed intervals. At pH 5.8, 65% of the sperm were motile at 2-4 minutes. Motility declined with time as sperm are only capable of remaining motile for a limited time. At pH 4.2 only 2.2% of sperm were motile at the 2-4 minute interval and at pH 3.2 non were motile. Sperm motility declined with time at all pH levels and with increasing acidity after any given time interval. Addition of sulphate (86 uM) further suppressed motility.

Spores were germinated on vermiculite and subsequently exposed to the buffers (pH 2.2 to 5.8). Sporophyte production, which indicates that fertilization has occurred, was assessed. Fertilization declined with increasing acidity. Addition of sulphate (86 uM) futher suppressed fertilization by 50% at all pH levels.

Sperm motility showed a normal distribution when plotted against pH while fertilization versus pH was linear. This suggested that sperm motility was the limiting factor in fertilization. Sulphate concentrations which were about twice that found in New York rain water can reduce sperm motility and fertilization.

Sperm flagellae react to acid conditions while vegetative structures may be unaffected. Under ambient conditions of acid rain fertilization may be suppressed.

This work indicates that reproduction in ferns may be reduced by acid conditions but it is not know how this would affect the population. Only a small percentage of sporophytes would survive competition. A selection for tolerant strains may occur under acidic precipitation conditions.

(3) Effect of Buffered Solutions and Various Anions on Vegetative and Sexual Development in Gametophytes of Pteridium aquilinum

L.S. Evans and D.M. Bozzone; Canadian Journal of Botany, Vol. 56, 1978, pp. 779-785

A previous paper (Evans and Bozzone 1977) discussed the effect of pH and a

single concentration of sulphate on sperm mobility and fertilization in bracken fern. Effects of other ions in varying concentrations are examined here.

Increasing acidity and sulphate concentrations reduced sperm mobility singly and in combination (pH range 5.8 to 4.2, sulphate concentration range 0-173.2 uM) after a 2-4 minute exposure. Concentration of Cl^- and NO_3^- equal to the $\text{SO}_4^{=}$ were tested. At pH 5.8, sperm mobility was higher in the presence of Cl^- when compared to $\text{SO}_4^{=}$ or NO_3^- . At pH 4.8 response to Cl^- was similar to NO_3^- . $\text{SO}_4^{=}$ had a greater affect at pH 4.8 than NO_3^- or Cl^- .

Fertilization decreased with increasing $\text{SO}_4^{=}$ concentrations at all pH levels (4.2 to 5.8) when compared to no sulphate controls. Using NO_3^- , $\text{SO}_4^{=}$ and Cl^- in various combinations indicated that these ions had similar effects, singly or in combination on fertilization at a given pH.

This work, together with a previous paper (Evans and Bozzone, 1977) shows that reproduction in ferns may be affected by environmental variables other than rainfall acidity.

(4) Volcanic Air Pollution: Deleterious Effects on Tomatoes

B.A. Kratky, E.T. Fukunaga, J.W. Hylin and R.T. Nakano; Journal of Environmental Quality, Vol. 3, 1974, pp. 138-140

Fumes from active and degassing vents of a volcano produced a haze over a tomato growing area in Hawaii. Plants suffered blossom drop, poor fruit set, hollow, small and almost seedless fruit and a less luxuriant appearance. The causal agent for this damage was investigated.

Plants grown beneath plastic rain shelters grew normally while plants without the shelter showed the symptoms of damage. Rainfall components were suspected as causal agents.

Rainwater analysis showed it to be a dilute solution of H_2SO_4 and HCl at pH 4, containing organic compounds in the ppb range. Rain from a neighbouring island had 1000 times less of the organics.

Since rain is known to leach nutrients from foliage, leaf discs were immersed in rainwater, distilled water and distilled water acidified (HCl) to pH 4.0 for 4 hours. The dilute HCl leached 2 or 3 times as much Ca, Mg, K as distilled water. Neutralizing rainwater to pH 5.7 with NaOH still caused greater leaching losses than distilled water. The polluted rain was causing abnormally high leaching of cations.

Since one of the symptoms of injury was seedless fruit, pollen germination and tube length was examined. Germination occurred in distilled water but not in

rainwater of pH 4.0. As pH of rainwater decreased so did germination and tube lengths. Dilute HCl (pH 4.0) also greatly reduced germination. Neutralizing rainwater with NaOH to pH 5.7 did not increase pollen germination. Organic compounds in rainwater are suspected for this inhibition.

It was also noted that samples from a single heavy rainfall was less acidic than samples from cumulative light rainfalls. The first increment of rain absorbs most of the pollutants and is thus more damaging to plants.

The cause of injury does not appear to be rainfall acidity. However, the experiments performed using dilute HCl demonstrated increased leaching losses and reduced pollen germination.

(5) Effects of Inorganic Components in Acid Rain on Tube Elongation of Camellia Pollen

N. Masaru, F. Katsuhisa, T. Sankichi and W. Yukata; Environmental Pollution (Series A), Vol. 21, 1980, pp. 51-57

The experiments described were designed to test the effects of acidic rain components on tube elongation of Camellia pollen. Pollen was sown onto sucrose and agar plates pre-treated with the acids HNO_3 , HCl or H_2SO_4 or with the metallic salts $\text{Pb}(\text{NO}_3)_2$, $\text{Mg}(\text{NO}_3)_2$ or $\text{Mn}(\text{NO}_3)_2$.

The effects of the combination of the acids or the combination of NH_4NO_3 , NH_4Cl and $(\text{NH}_4)_2\text{SO}_4$ were also examined.

Low concentrations of acids promoted tube elongation but inhibition occurred above an acid concentration equivalent to pH 3.2. The Pb and Mg nitrate treatments promoted tube elongation at low concentration (0.005-0.015 mM). $\text{Mg}(\text{NO}_3)_2$ did not show this effect.

When the 3 acids were combined in equal proportions, the effect was essentially identical to the effect of the sum of the individual treatments. The ammonia salts treatment showed neither promotion or inhibition.

These experiments demonstrate the role of H^+ concentration in pollen tube elongation. Acids in low concentrations promoted elongation while neutral salt equivalents of the acid anions did not show the effect. However, the magnitude of the effect of the three acid anions differed.

The additive, inhibitory effect of the 3 acids suggests that H^+ ions are deleterious to pollen tube elongation, but only when pH is less than 3.2.

F. HOST - PARASITE INTERACTIONS AND NITROGEN FIXATION

Plant pathogens usually require water as a medium for infecting plants. If the water is acidic, as may be the case if the precipitation is acidic, then acid sensitive pathogens may be inhibited. Conversely, if acid damage to plant tissue has occurred, then the pathogen may have acquired an infection pathway.

Nitrogen fixation can be accomplished by free-living organisms such as lichens, or by organisms associated with root nodules on leguminous plants. Acidic precipitation or soil percolate may inhibit nodulation or nitrogen fixation.

Studies of these two types of acidic precipitation-vegetation effects are uncommon and consist of experimental studies. More effort has been directed to examine effects on soil microorganisms. These are summarized elsewhere in this bibliography.

(1) The Effects of Acid Rain on Nitrogen Fixation in Western Washington Coniferous Forests

R. Denison, B. Caldwell, B. Bosmann, L. Eldred, C. Swanberg and S. Anderson; Water, Air and Soil Pollution, Vol. 8, 1977, pp. 21 - 34

This paper reports on a study of the effects of applications of acid solutions on nitrogen fixation by free living soil microorganisms and lichens. The method used consisted of examining the rates of acetylene reduction to ethylene. Observations on effects on soil microorganisms are reviewed elsewhere in this bibliography.

Needles of Douglas fir support a community of algae, fungi, bacteria and microlichens. Acetylene reduction was observed when needles were exposed to a gas mixture of acetylene, argon and oxygen. The rate was lower when the oxygen was omitted. Scrapings of the microflora from the needles were also shown to fix nitrogen. No attempt was made to test the effect of pH on N-fixation by this component of the ecosystem.

The epiphytic lichens Lobaria pulmonaria and L. oregana are also known N-fixing organisms. It was determined that L. oregana fixes nitrogen at a rate 1000 times that of litter and 10,000 times that of soil.

The role of acidity in affecting the N-fixing capabilities of the two lichen species was examined. Dried fragments of the lichens were soaked in distilled water and N-fixation rates determined. This experiment was followed by a soaking in water with pH adjusted to 8, 6, 4 or 2 with NaOH or H_2SO_4 and fixation rates compared to the distilled water soak. Fixation was highest at pH 8 and declined

with increasing acidity. Samples were re-dried and soaked in distilled water. The pH 2 treatment had a severe and permanent effect on the N-fixing capability of the lichens.

The relative contribution of litter, soil and lichens to N-fixation in the ecosystem are compared. It was shown that L. oregana is the largest contributor to fixed nitrogen in the ecosystem.

Acidic precipitation or SO_2 can have a significant deleterious effect on N-fixation by this species.

It would have been advantageous if some attempt had been made to measure the stemflow pH at the study site. This could have provided an estimate of current effects on the lichens by acidic precipitation.

(2) Effects of Simulated Acid Precipitation on Nodulation of Legumes by Rhizobium spp

D.S. Shriner; Proceedings of the American Phytopathological Society (Annual Meeting, 1974), Vol. 1, 1975, p. 112, (abstract)

This abstract summarizes Shriner and Johnston (in press).

(3) Effects of Acidic Precipitation on Host-Parasite Interactions.

D.S. Shriner; Proceedings of the American Phytopathological Society (Annual Meeting, 1974), Vol. 1, 1975, p. 114, (abstract)

This abstract summarizes Shriner (1978).

(4) Effect of Simulated Rain Acidified with Sulphuric Acid on Host-Parasite Interactions

D.S. Shriner; Water, Air and Soil Pollution, Vol. 8, 1977, pp. 9-14

This paper is a summary of experiments examining effects of acid rain on plant-parasite interactions (Shriner 1978) and on nitrogen fixation in leguminous plants (Shriner and Johnston in press).

These papers are reviewed elsewhere in this bibliography.

(5) Effects of Simulated Acidic Rain on Host-Parasite Interactions in Plant Diseases

D.S. Shriner; *Phytopatholgy*, Vol. 68, 1978, pp. 213-218

Many bacteria and certain fungi have growth and reproduction inhibited under acidic conditions. Acid rain may affect parasitism by plant pathogens.

Plants were sprayed with a simulated rain solution acidified by H_2SO_4 to pH 3.2 (control pH was 6.0). Several host-pathogen systems were investigated. Acid rain treatments and parasite inoculation procedures were variable, depending on the system under investigation.

Willow oak seedlings were treated by the acid rain before, during and after inoculation by Cronartium fusiforma (oak-pine rust). Forty-two percent fewer leaves were infected while infected leaves had 80% fewer telia than with control rain. Acid treated leaves developed lesions.

Corn was not pretreated with acid but post-inoculation treatments were with pH 3.5 or 7.0 simulated rain. Inoculation was made in acid or control media, i.e. acid inoculation was followed by acid or control treatment, control inoculation was followed by acid or control treatment. Two corn strains were investigated. Inoculum was Helminthosporium maydis (southern corn blight).

Regardless of inoculum pH, the number of leaves per plant that died following post-inoculation treatment by pH 3.5 rain was the same for both strains. Response of plants treated by pH 7.0 post-inoculation rain varied with the strain but not with inoculum pH. Greatest differences occurred between pH 3.5 and 7.0 post-inoculation treatment with one of the strains.

Pre-inoculation treatment of bean with pH 3.2 rain resulted in more halo blight leaf death (Pseudomonas phaseolicola). Inoculation in acid rain did not produce disease symptoms. Post inoculation treatment by pH 3.2 rain reduced infection.

pH 3.2 rain inhibited reproduction of Meloidogyne hapla (root-knot nematode) on kidney bean. Root galling was also reduced. Bean rust (Uromyces phaseoli) infection was delayed by pH 3.2 treatments.

The bean halo blight bacteria (P. phaseolicola) was inhibited by the acid during and after inoculation. Pre-inoculation acid treatment predisposed plants to infection possibly by creating pathogen penetration avenues.

Reduced infection of willow-oak through acid treatment suggests that acid reduces susceptibility to infection or directly affects the pathogen.

It is unlikely that the root knot nematode would be affected directly by the acid as it is within the root tissue of kidney bean. The pH 3.2 treatment may have affected plant physiology or directly affected free living stages of the nematode.

These experiments demonstrate that rainfall acidity may affect host parasite relations. Effects of acid rain on host-parasite relations will depend on the treatment and inoculation procedure. Acid rain induced plant injury may provide entry pathways for the pathogen. Disease may be inhibited if the pathogen is in contact with the acid rain and is sensitive to acidity.

(6) Effects of Simulated, Acidified Rain on Nodulation of Leguminous Plants by Rhizobium spp

D.S. Shriner and J.W. Johnston; Soil Biology and Biochemistry (in press)

This series of experiments was designed to determine if acidified rain could; 1) affect growth and nodulation of leguminous plants, 2) affect nodulation by inducing changes in the plants, soil or both, 3) induce changes in nitrogenase activity of the nodules, 4) induce nodulation effects as a function of plant age at treatment, and 5) alter the capacity of various soils to support nodulation with or without liming.

The test plants used were field grown Phaseolus vulgaris (kidney bean) and field and greenhouse grown Glycine max (soybean). Rhizobium was the inoculum. The rain solutions consisted of deionized water at pH 6.0 and deionized water acidified by H_2SO_4 to pH 3.2.

"Rain" application in the greenhouse was a daily 10 minute treatment averaging 0.63 cm per day over 5 weeks. Productivity, nodulation and nitrogenase activity were examined.

Addition treatment variations in the greenhouse included rain application to soil or foliage only, application to plants of different age and soil liming.

In all experiments, plants receiving the acid rain produced fewer nodules and fewer plants nodulated. The mass of individual nodules was not different so development was not affected once nodulation was initiated. No consistent differences were observable in plant productivity (field and greenhouse) and soil and tissue chemistry (field).

Acid application in the greenhouse lowered soil pH by 0.9 units to below 5.0. Since nodulation is inhibited in soil below pH 5.0, soil acidity may be responsible for the observed reduction in nodulation.

Nodulation was reduced where pH 6.0 rain was applied to foliage only, as compared to soil application only. A stress-induced imbalance in carbohydrate allocation is postulated.

Reduced nitrogenase activity (as measured by acetylene reduction) in plants subjected to pH 3.2 rain is a result of a reduction in the number of nodules formed

per root system.

Rain at pH 3.2 reduced nodulation irrespective of time of exposure. As exposure duration increased, nodulation decreased. Plants did not recover if acid rain application ceased.

Lime additions reduced nodulation inhibition in some soil types. Nodulation of plants growing in soil with a high CEC did not respond to liming. High Al concentrations in acidified clay soil may reduce phosphorous uptake.

The pH values used, 3.2 and 6.0 represent extremes of rainfall acidity. Threshold pH predictions are not possible, nor is it certain whether H^+ or $SO_4^{=}$ is responsible for the effect. While growth and yield was not affected in these experiments, the reduced nodulation may cause reduced productivity under prolonged exposure to acid rain.

From the observations made in these experiments it appears that nitrogen fixation by leguminous plants will decline under acid soil conditions. This is then one of the deleterious possibilities under an acidification trend. However, under normal agricultural liming practices, there is unlikely to be a noticeable effect on crop productivity.

G.

MISCELLANEOUS - VEGETATION

This section contains those publications that could not be allocated unambiguously to one of the previous sections. They do, however, have relevance to acidic precipitation effects on vegetation.

This section also contains research or literature reviews considering a number of aspects of acidic precipitation effects on vegetation. More general reviews, containing both soil and vegetation aspects, are summarized in the Reviews and General Papers section.

(1) Effects of Acid Precipitation on Coniferous Forests

G. Abrahamsen, K. Bjor, R. Horntvedt and B. Tveite; In: Impact of Acid Precipitation on Forest and Fresh Water Ecosystems in Norway, F.H.Braekke (ed), SNSF - Project, Research Report No. 6, 1432 Aas-NLH, Norway, 1976, pp. 37-63

This report is a summary of results from the first phase (1972-75) of the SNSF project. The chapter by Abrahamsen et al, Effects of Acid Precipitation on Coniferous Forests is examined here.

The alterations in chemistry of precipitation in throughfall was given in Bjor et al (1974). The observed leaching of cations seen under these natural conditions was further examined in the simulation experiments described in Abrahamsen et al (1976). The pH of the simulated rain significantly affected amounts of Ca, Mg and K in throughfall under spruce. Ca and Mg was absorbed by the trees from water of low acidity. At pH 3 and lower, Ca and K were lost from foliage. K was lost throughout the pH range of treatments with an increase at lower pH. Since spruce did not exhibit foliar injury, the leaching could not be attributed to dead cells.

Injury, as foliar lesions, was observed on birch, willow herb and Scots pine at pH 2 and 2.5 and on mosses at pH 3.0 and less. Species diversity and cover of understory plants declined under acidic treatments.

Studies of seed germination and seedling survival and comparisons of tree growth by the tree ring analysis from different regions of Norway are presented. These were summarized in Abrahamsen et al (1975)

Growth of trees in the field plots receiving simulated acid rain was examined. Height growth under acid treatment was related to the control treatment. No negative influence to growth was observed during the experimental period of 1 to 3 years. Twenty percent stimulation of growth was observable for lodgepole pine receiving 50 mm/mo "rain" at pH 3 and 4. Norway spruce did not show any response to acidity of treatments.

The short term of this experiment may be insufficient to evaluate effects on productivity. However, loss of soil and foliar nutrients and increasing soil acidity are a potential threat to forest ecosystems.

This report summarizes previous reports in the SNSF FR series (Research Reports) but also presents information from the as yet unpublished (as of 1976) report. Some discussion of the literature is also presented.

(2) Nutrient Levels in Rainfall, Lodgepole Pine Foliage and Soils Surrounding Two Sulphur Gas Extraction Plants in Strachan, Alberta
J. Baker; Information Report NOR-X-194, Fisheries and Environment Canada, Canadian Forestry Service, 1977, 18 p.

Analysis of rainfall, foliage and soil collected in the vicinity of sulphur gas extraction plants was conducted. Rainfall pH was not different between exposed and control sites, however S was elevated closer to the plants. pH of the rain from all sites was greater than 5.6 and neutralizing agents were suspected.

S and Al content of the pine foliage was higher at the SO₂ impinged sites with Ca, Mg and P levels lower. No consistent trends could be noted for Fe, K, Na and N. Elevated S can be accounted for by SO₂ absorption by the foliage while Al would be made more available in the acidified soils which occurred at the exposed sites. Reduced Ca and Mg levels are attributable to depletion in the soil while reduced P is possibly due to immobilization by elevated soluble soil Al.

Observations on changes in soil chemistry are reviewed elsewhere in this bibliography.

While this report cannot be regarded as a report on the effects of acid precipitation, it does demonstrate the potential and commonly predicted effects of acidification of the terrestrial environment.

(3) Effects of Acid Precipitation and Atmospheric Deposition on Terrestrial Vegetation
E.B. Cowling; In: A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain), A Report to the Council on Environmental Quality, National Atmospheric Deposition Program, NC-141, 1978, pp. 46-63

The problem of potential detrimental effects of acidic precipitation on vegetation is reviewed together with other forms of atmospheric pollution such as pollutant gases and particulates.

Since rain may contain beneficial or harmful substances in solution the net effect on vegetation will depend on the chemical composition, duration and intensity of the precipitation event as well as the species and physiological condition of the organisms. Some substances may be beneficial at low concentrations but become toxic at high concentrations. Since rain consists of numerous cation or anions other than H^+ ions, and the composition is variable, it is difficult to assess the impact of the acidity in isolation from the general chemistry.

A list of potential effects of acid precipitation originally prepared by Tamm and Cowling (1976) is reproduced. This list has been summarized elsewhere in this bibliography. The net result of such effects would be a decrease in growth but such has not been demonstrated in natural ecosystems. Most of the effects have been demonstrated through laboratory or field experiments.

Atmospheric deposition is an important source of nutrients to forests which are not fertilized by man. The large surface area of forest canopies is an effective mechanism of intercepting both beneficial and injurious substances from the atmosphere.

Human activity is becoming a major force in the biochemistry of the earth. The injection of pollutants into the atmosphere at high altitudes disperses the pollutants over wide areas. Increased surveillance of atmospheric deposition is necessary.

This paper proceeds to review the phenomenon of increasing precipitation acidity, examines the research being conducted and the international meetings held to assess the problem. The findings of researchers using simulated acid rain to assess vegetation response is also given.

Some priorities for future research on effects of acid precipitation are suggested. These include: 1) determine spatial and temporal distribution of nutrient and injurious substances in precipitation; 2) determine quantitative contribution of nutrients through deposition and foliar absorption; 3) determine extent of cuticular erosion by acid rain; 4) determine pathway of foliar absorption of nutrient elements; 5) determine influence of atmospheric deposition on heavy metal content of crops; 6) determine influence of acid precipitation on nutrient cycling; 7) identify susceptible life forms, stages and processes; 8) use ecosystem approach to assess effects on productivity and species diversity; 9) determine dose response relationships; 10) determine influence of acid substances in snow on over-wintering of crops such as spring wheat and effects on nitrogen-fixing algae and free living bacteria.

(4) Predicting Potential Impacts of Acid Rain on Element Cycling in a Southern Appalachian Deciduous Forest At Ceweeta

B. Haines and J. Waide; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 335-390

Exposure of ecosystems to acid rain may disrupt nutrient cycling. An understanding of the magnitude and consequences of such a disruption is necessary in the formulation of management strategies.

The approach is to characterize the response of leaves, roots and soil to artificial acid rain simulations. Leaching from leaves and soil and uptake by roots will be evaluated under differing acid simulation regimes. Movements of Na, K, Ca, Mg, NH_4 , SO_4 , NO_3 and Cl will be assessed.

This paper summarizes proposed experimentation; no data are presented. This approach separates ecosystem components and examines effects of acid precipitation simulation on nutrient flux in or out of the compartments.

(5) The Effect of Simulated Acid Rain on Seedling Emergence and Growth of Eleven Woody Species

J.J. Lee and D.E. Weber; Forest Science, Vol. 25, 1979, pp. 393 - 398

The effect of simulated acidic rain on seed germination and seedling growth are the object of this study. A soil mixture consisting of topsoil, silica sand and pea gravel was placed in flats and sown with a mixture of seeds from eleven different woody plant species. The seeds were covered with a mulch and the beds placed out of doors under a translucent cover to exclude ambient rain.

The test solutions contained ionic constituents approximating ambient rain at Hubbard Brook N.H. (pH 5.7). The solutions were also acidified with H_2SO_4 to pH 4.0, 3.5 or 3.0. A nozzle system applied the solutions at a rate of 2.5 mm/hr for 3 hrs/day, 3 days/week. The experiments lasted 5 to 7 months at which time the emerged seedlings were harvested and dry weights of roots and tops were determined.

The general observations suggest that there is a nonmonotonic response to acid rain suggesting competing stimulatory and inhibitory effects. Mild acids are used in silviculture to scarify seed coats, while sulphate absorbed by leaves may have a fertilizing effect. Conversely, growth inhibition can occur if sulphate accumulates to toxic levels or if there is foliar injury.

Five of the species showed a germination response to acid. Staghorn sumac

was stimulated while eastern white pine, eastern red cedar and yellow birch were inhibited. Douglas fir response was mixed.

No species showed reduced top growth under acid treatment. Top growth of Douglas fir and shagback hickory was stimulated. Sugar maple and tulip-poplar response was mixed. The only species with significant root weight reduction under the acid treatments was staghorn sumac.

Since the soil used in these experiments was a strong sulphate absorber, the effects on growth were probably due to direct foliar interaction. Effects on emergence rate and growth rate were unconnected.

Eight out of the 11 species were affected by the simulated acid rain at pH 4.0 or lower. This suggests that the rain currently falling on the N.E. U.S.A. has an acid concentration high enough to affect germination and seedling growth of forest species.

These experiments demonstrate that there is still much ambiguity as to negative or positive influence of acidic precipitation on forest species. No consistent trend was demonstrated. This paper did not mention any observable foliar injury, even at the prolonged pH 3.0 treatment level. Nor was soil mix pH reported, although the topsoil used in the mix had a pH of 5.4. Soil conditions would be more important to germination success as opposed to treatment solution pH. The mulch would have certainly altered the pH of the treatment solutions.

(6) Acid Rain - A Plus or Minus to Agriculture

R.A. Pennay; Unpublished manuscript, U.S. Department of Agriculture, Harrisburg Pennsylvania, 1980

It is known that when the pH of soil falls below 6.0, fertilizer efficiency and crop yield decline. The precise mechanism for this effect is ill-defined. The effect of acid rain on agricultural soils has not been fully determined. The U.S. E.P.A. work (Lee *et al* 1980) is cited to have produced both positive and negative growth response to simulated acidic rain.

The deposition of sulphur and nitrogen to agricultural land would be beneficial from a cost perspective because neutralizing the associated acids would be less costly than the benefit realized from this fertilization. The acid from atmospheric sources is small in comparison to that generated through fertilization or vegetation decay.

The location of agricultural lime sources and soil pH maps for Pennsylvania are presented.

While the net effect of acid rain to agriculture may be a benefit, the same

may not be true for natural ecosystems.

(7) Acid Rain: A Factor Contributing to the Paucity of Epiphytic Cryptogams in the Vicinity of a Copper Smelter

G. Robitaille, F. LeBlanc and D.N. Rao; *Revue Bryologique et Lichenologique*, Vol. 43, 1977, pp. 53-66

It is generally assumed that epiphytes are most affected by gaseous air pollutants. Rainwater after interacting with the bark substrate will flood the lichens and its properties may affect lichens. Rainwater in vicinity of SO_2 sources will scavenge SO_2 and will be acidified by sulphurous acid. pH and buffering capacity of bark may be affected and in turn affect epiphytic lichens.

pH and buffering capacity of bark, pH and S content of stemflow and incident rain, SO_2 concentrations and pH of lichen thalli were assessed. SO_2 besides affecting epiphytes as a gas will also play an important role when dissolved in rainwater. Bark in SO_2 polluted areas was more acid and had lower buffering capacity, resulting in deleterious affects on epiphytes.

It is hypothesized that bark pH is not dependent upon pH of incident rainfall but dependent upon pH of stemflow. Factors regulating sensitivity of epiphytic lichens in SO_2 polluted areas appear to be relative concentrations of sulphurous acids and bisulphite ions in the stemflow.

It is concluded that factors determining sensitivity of epiphytic communities to SO_2 pollution in order of importance are: ambient SO_2 concentration, stemflow pH, bark pH, epiphyte pH, buffer capacity of bark and relative percentages of SO_2 derivatives (bisulphite ions and sulphurous acid) in and around lichen thalli.

This study was conducted in the vicinity of an SO_2 emitting source. The attempt was to relate lichen sensitivity to SO_2 derivatives in water interacting with lichen thalli and it was found that these were low on the list of importance. Acid precipitation may have deleterious effects on lichens by altering bark and stemflow chemistry.

(8) Effects of Acids on Forest Trees as Measured by Titration in vitro, Inheritance of Buffering Capacity in Picea abies

F. Scholz and S. Reck; *Water, Air and Soil Pollution*, Vol. 8, 1977, pp. 41-45

Metabolic processes in plant cells depend on some optimum pH, maintained by regulation. The effectiveness of the regulation mechanism may impart varying

degrees of resistance to exogenous influences such as acidic precipitation. Determination of the buffering capacity of homogenized tissue by titration can be used to test this regulation.

Earlier experiments showed the differences exhibited by 3 pine species to buffer NaOH. The genetic background of buffering capacity in Picea abies is examined.

Clones exhibited differences in capacity to buffer HCl, suggesting genetic differences. Buffering capacity of parents and offspring were correlated.

Physiology of plant tissue will be affected through acidification of cytoplasm. These experiments suggest that resistance to pH change may relate to susceptibility to acidic precipitation.

(9) Simulated Acid Rain on Growth and Cadmium Uptake by Soybean

J. Shen - Miller, M.B. Hunter and J. Miller; Plant Physiology: Annual Meeting Supplement, Vol. 57, 1976, p. 50, (abstract)

Simulated sulphuric acid rain was applied to the tops of soybean plants for 4 weeks. Apparent increase in top growth and reduced root growth were not significant in the pH range neutral to 2.1 Injury was correlated with treatment acidity.

Cadmium uptake was enhanced in acid treated plants. The method of Cd application is not disclosed but there is an implication that it was applied as a solution to the leaves. A 10 ppm Cd treatment caused significant necrosis in acid treated plants. Necrosis also occurred in areas not treated with Cd.

It is suggested that acid rain stressed plants may be more susceptible to other pollutants, such as Cd in fly-ash, resulting from changes in cell wall and membrane structure.

(10) Some Effects of Rain and Mist on Plants with Implications for Acid Precipitation

H.B. Tukey, Jr.; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.C. Hutchinson and M. Havas (eds), Plenum Press, New York, 1980, pp. 141-150

Rain, mist and dew are capable of leaching a wide variety of substances from foliage including inorganic nutrients, essential minerals, macro and micro elements and various organic substances including plant hormones.

Of the inorganic nutrients, K, Ca, Mg and Mn are usually leached in greatest

quantities. Carbohydrates also account for a great quantity of leached material.

Factors influencing leaching are associated with the plant itself and the environment. Aside from species differences, leaves of different physiological age will be leached to differing extents. Actively growing tissue is less prone to loss of nutrients and carbohydrates via leaching. Leaf surface texture also influences leaching. Pubescent leaves which are easily wetted are more prone to leaching than leaves with a thick waxy cuticle. Plants injured by pathogens, adverse climate or nutritional and physiological disorders will be prone to leaching. Injury by acid in rain will also contribute to leaching losses.

Leaves need only be wetted to be leached. Increasing the volume of leaching solution has little effect on quantity of material lost. Continuous leaching over extended periods of time can result in losses that exceed initial tissue concentrations. Root adsorption and translocation continuously replaces losses from foliage.

Cations are leached from exchangeable pools in the "free-space" areas in plants. Losses from cells are not substantial. Cations are lost by exchange with H^+ ions in the leaching solution or by diffusion and mass flow into the solution. By combining with dissolved CO_2 , they form alkaline carbonates on the leaf surface. Consequently, anions need not be leached from plants.

Young, vigorously growing tissues will have lesser amounts of cations in the exchangeable pool and more accumulating within cells. In older tissue, cellular assimilation is reduced and there are accumulations in excess of metabolic requirements.

Leaching from foliage constitutes an important nutrient cycling pathway in natural ecosystems. Nutrients are thus delivered to understory plants. Leaching of inhibitors can suppress competition by other plants. Nutritional value of food crops can be reduced. Losses of sugars will affect fall colour development or initiation of winter dormancy. It is important to consider such effects when assessing the role of acid precipitation on plant growth.

This paper reviews the importance of leaching in regulating or influencing plant processes. The potential alterations to such processes by acid precipitation are not discussed. The most likely effect may be a depletion of nutrient cations by excess H^+ ions and plants may suffer nutrient deficiencies.

SOIL SECTION

Table of Contents

- A) Mobilization of Elements in Soil**
- B) Soil Susceptibility to Acidic Precipitation**
- C) Effect of Acidification on Soil Microorganisms**
- D) Effects of Acid Precipitation via Soils on Aquatic Systems**
- E) Acidification of Soils by Acidic Precipitation - Marginal Examples**
- F) Reviews and General Papers on Acidic Precipitation and Its Effect on Terrestrial Ecosystems**

A. MOBILIZATION OF ELEMENTS IN SOIL

Papers which offer information on the movement of cations (Ca, Mg, K, Na), anions (SO_4 , PO_4 , H^+) and soil-bound metals (Al, Fe, Mn) as a consequence of acidified precipitation are reviewed in this section. The research undertaken by the authors includes work with the soil in-situ under natural acidic precipitation regimes, simulated acid rain experimentation and pedological theories and modeling. Consensus in the literature seems to be that leaching of cations and Al could occur in the soil over a few decades if the acidity of rainfall is less than 4 and the soils are slightly impoverished and strongly buffered. It has been suggested that cation leaching may not occur unless SO_4 is mobile in the soil or it displaces another anion that is mobile in the soil. Since mobilization of cations, anions and soil-bound metals appears to be the initial change in the soil when exposed to acidic precipitation there are many papers on this topic and hence this is the largest section of the soil's portion of the bibliography.

(1) Field Experiments with Simulated Acid Rain in Forest Ecosystems

G. Abrahamsen, K. Bjørn, O. Teigen; 1. Soil and vegetation characteristics, experimental design and equipment, SNSF-Project, Research Report No. 4, 1432 Aas-NLH, Norway, 1976, 15p.

This paper presents a description of field experiments and is an introduction to a series of reports of experiments with simulated acid rainfall in forest ecosystems. According to the authors the aim of these experiments is to elucidate the effect of acid precipitation on tree growth, ground cover, vegetation and on chemical and biological properties of soil. Preliminary results of one of these experiments were given by Abrahamsen *et al* (1975) FR 2/75.

The experiments are established in young plantations of Norway spruce, Lodgepole pine, Scots pine and birch, and also in a mature stand of Scots pine. The study areas are flat plains of glaciofluvial sediments deposited above the marine limit overlying Precambrian and Permian crystalline bedrock. The deposits are dominated by sand and are exceedingly thick (up to 60 m). The soils are iron podzols with pH's ranging from 3.7 to 5.4.

Field plot size varies from 15 to 625 m^2 and the number of replicates from 3 to 10. During the growing season 25 or 50 mm/mo of simulated acid rain with pH levels ranging from 2.0 to 6.0 is applied once a month. The authors explain that the simulated rain is obtained by adding H_2SO_4 to well water. The fact that ground water is used as the base for the simulated rain was omitted in FR 2/75

Abrahamsen et al. Although a table providing information about the chemical composition of the groundwater is found in this report the authors do not state how often the groundwater is tested, if chemical variations occur over the year, or year by year. The 5 experimental plots are spread out over 3 different sites, each with a different groundwater chemistry. The authors are aware of the variation in groundwater quality between sites but do not offer an explanation as to how the difference will be accounted for in their experiments.

The irrigation equipment at each site is described in detail. The pumps were constructed especially for these experiments using noncorrodible plastic material. The method for mixing H_2SO_4 with the groundwater differs from site to site and might possibly account for some differences found between sites later on.

(2) Impacts of Acid Precipitation on Coniferous Forest Ecosystems

G. Abrahamsen, R. Horntvedt and B. Tveite; SNSF-Project, Research Report No. 2, 1432 Aas-NLH, Norway, 1975, 15p., also in: Water, Air and Soil Pollution, Vol.8, 1977, pp.57-73

This paper summarizes the 3 years of results from Norwegian studies which commenced in 1972. Artificial acid "rain" and lime were applied to field plots and lysimeters. Rain water quality was adjusted with H_2SO_4 and applied once a month at pH 3.0, 4.0 and 5.7 at the rate of 25 mm/mo and 50 mm/mo. The soil and vegetation were not shielded in any way from the natural precipitation. Nowhere in the report does it explain how the acid rain is made, ie. whether it has a distilled water or groundwater base or if acid "rain" was composed in the laboratory. The leachate was stored in the field and preserved with 10 ml of HCl and analyzed once a month.

Sandy semi-podzolic soils were used in the study. Unfortunately the term "semi-podzolic" is not clearly defined in the report. Effects of rain acidity were only observed in the field where no lime was added and at the "rain" level of 50 mm/mo. "Rain" of pH 3.0 resulted in a significant reduction of base saturation. Acid rain applied at the rate of 25 mm/mo to lysimeters increased the leaching of Ca and Mg. (These data are displayed using relative figures, the amount of Ca leached at pH 5.7 in 1973 being equal to 1.0 which makes comparison to results from other sources infeasible). Increased leaching of nitrate, organic nitrogen and other cations have not been observed at this level. Significant increases in leaching of cations had occurred when rain amounts increase and especially when the rain becomes more acidic than pH 3.0.

Two species of the soil enchytraeid fauna were not affected by the

application of acid rain. One species decreased in abundance with increasing acidity at a low lime level and increased in abundance at a higher lime level. These experiments indicate that severe negative influences on soil organisms are not to be expected over a period of a few years when the acidity of the rain is above pH 4.0.

Laboratory experiments revealed that decomposition of Lodgepole pine needles was not affected by acid rain. Liming slightly retarded their decomposition. No nitrification occurred on unlimed soils (pH 4.4-4.1) while liming increased this process.

Germination of Norway spruce seeds in acidified mineral soil was only affected when soil pH was 4.0 or lower. Seedling establishment was even more sensitive to increased soil acidity.

Analysis of throughfall and stemflow water in southern Norway revealed that the total deposition of H_2SO_4 beneath Norway spruce and Scots pine is approximately 2 times the deposition in open terrain. Increased rain acidity seems to increase leaching of cations from tree crowns.

Tree ring analyses of spruce and pine have been based on comparisons between regions differently stressed by acid precipitation and also between sites supposed to differ in sensitivity to acidification. This work closely paralleled that by Jonsson and Sundberg (1972) in Sweden. However, unlike Jonsson and Sundberg, Abrahamsen et al detected no difference in diameter growth that could be related to acid precipitation.

(3) Interaction Between Simulated Rain and Barren Rock Surface

G. Abrahamsen, A. Stuanes, K. Bjor; Water, Air and Soil Pollution, Vol. 11, 1979,
pp. 191-200

FA 34/78

The authors are concerned with the relationship between the chemical composition of simulated rain and that of run-off from bare granitic rock, partly covered by lichens. This study is part of a series of investigations on the effect of acid precipitation on fresh water chemistry.

The simulated rain was applied at the top of a slope using a polyethylene pipe. The run-off was collected 15 m farther down by means of a funnel formed from a polyethylene sheet stuck to the rock with screws and glue. The simulated rain took 3 minutes to travel from the top of the slope to the sheets.

When supplying simulated rain with a pH value of approximately 5.0 the very first run-off had pH values between 4.1 and 4.3. However, the pH in the run-off

increased rapidly and leveled out at values between 4.6 and 4.7. When supplying simulated rain with pH approximately 3.5 the pH in the first run-off varied between 3.8 and 3.6. The pH then gradually decreased to the same values of those in the simulated rain. Run-off from the simulated "rain" with pH 4.3, obtained the same pH value as that of the rain. The pH of the run-off was dependent not only on the rain acidity, but also on its content of neutral salts.

These experiments have demonstrated that the chemistry of simulated rain water was influenced when flowing over a granitic surface partly covered with lichens. The rock/lichen surface buffered the water towards a pH value between 4.1 and 4.3; however, this buffering was limited. After a few mm of simulated rain an equilibrium between this rain and the rock surface had been achieved and the run-off quality became very similar to the quality of the simulated rain. It was also demonstrated from the experiment the day after a night with heavy rain, that the run-off quality is likely to be influenced by previous rain episodes. From budget calculations where increased H^+ concentrations are accompanied by a decrease in concentration of other cations and vice versa, it seems likely that ion exchange is the most important process which may be used to explain the results obtained.

(4) The Acidification of Soils

B.W.Bache; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.183-202

Bache introduces the subject of acidification of soils by stressing that acidification is a natural and continuous soil process. The bulk of the report describes the principles of soil acidification and the factors that affect it.

The processes leading to soil acidification according to Bache are: 1) carbonic acid formation from CO_2 derived from the respiration of soil flora and fauna; 2) mineral acid generation by nitrification; 3) organic acid produced during the process of plant residue decomposition; 4) oxidation of pyrite (FeS_2); and 5) inputs of acidifying substance from the atmosphere.

Some effects of acidification of soils are: 1) loss of base cations; 2) reduction of cation exchange capacity; 3) mobilization of aluminum ions; 4) changes in biological activity.

The exchange of Al^{3+} for Ca^{2+} and Mg^{2+} , as well as exchange of H^+ for Ca^{2+} were considered in some detail. Bache stressed the importance of identifying the solution component of the soil acidity as the activity ratio $Ca^{++} (H^+)^2$, rather than the hydrogen ion alone. A simple comparison between the lime potential of the soil

and that of rainfall will show the direction of change of exchange equilibria by acid solutions. The extent of the change in the soil depends on: 1) the base saturation; 2) cation exchange capacity; 3) the relative bonding strength of the soil materials for hydrogen and basic cations.

In addition Bache considered the mechanism of movement of water in the soil.

Bache agrees with Wiklander's (1973/74) findings that for soils of high pH, a small decrease of pH is not of great biological significance and for strongly acid soils a further soil acidification is unlikely to occur because ion exchange is limited and the H^+ ions thus remain in solution and drain away. However, there is an intermediate range of susceptible, slightly acid, poorly-buffered soils where relatively little acidification may lead to striking loss of productivity.

(5) Impact of Acid Precipitation on Forest and Freshwater Ecosystems in Norway
F.H. Braekke, (editor); SNSF-Project, Research Report No. 6, 1432 Aas-NLH, Norway, 1976, IIIp.

This report is intended as a summary of the results of Phase I of the SNSF project covering the period July 1972-December 1975. The authors stress that many of the results are of a preliminary nature, and that many investigations in progress are not reported.

The report consists of 5 parts. First, the research director presents a synthesis of the report. The substance of the report was written by senior scientists, associated with the project, in four summary articles. The subject matter includes the deposition of pollutants, the effect of acid precipitation on coniferous forest, the chemistry of freshwater and the effect of acid precipitation on fresh water organisms.

General Introduction and Synthesis

L.Overrein pp.9-12

Overrein, the research director, presents a brief account of the effect of acid precipitation on terrestrial and aquatic ecosystems. He adopts a systems approach to this research emphasizing that a dynamic equilibrium exists between soil, water, the atmosphere and living organisms.

The geographical distribution of wet deposition of southern Norway is described and presented in a map (Figure I). A zone of maximum acid precipitation is found along the south coast where the mean annual pH is 4.3. About two thirds

of the acid is sulfate and one third nitrate.

The effect of acid precipitation on aquatic species is outlined concisely. It appears to be a summary of SNSF report 5/76 by T.Gjedrem.

The soil information is summarized and Overrein states that Norwegian forests are characterized by podzol and peat soils, which are highly leached and consequently low in exchangeable cations. The experiments involving soils and simulated acid rain and the tree ring studies are described in general.

Overrein stresses that the effects on terrestrial ecosystems are subtle and difficult to document over the short term, but may be serious over the long term when remedial action may come too late.

Deposition of Air Pollutants in Norway

H.Dovland, E.Joraner and A.Semb pp.15-35

The geographical distribution of the wet deposition of sulfate and acid in Norway and the long term changes in precipitation quality are outlined in this section. Estimates of dry deposition based on dispersion model calculations are also included.

The locations of precipitation sampling stations (daily, weekly, monthly) are provided in map and table form. The monthly samples are analyzed for SO_4 , NO_3 , NH_4 , Cl, Na, Ca, Mg, pH, HCO_3 , electrolytic conductivity and titratable acid. The yearly mean pH, sulfate and nitrate for these stations indicated a significant decrease in mean pH and an increase in mean sulfate and nitrate during the period 1955-1973.

Measurements and model calculations show that the deposit of sulfur compounds in Norway is two to three times the amount of its own emissions. Most of this deposition occurs during "episodes". The distribution of wet deposition in Norway reveals a maximum zone of acid precipitation along the southern coast, where the annual mean pH is 4.3 and the annual mean deposition of sulfate is 4 g SO_4/m^2 . The main causes of this deposition are enhanced precipitation and scavenging of air pollutants due to orographic effects with southerly winds and transportation of air masses from regions with large anthropogenic emissions. The geographic pattern of mean concentration of ammonium and nitrate are similar to the distribution of sulfate.

In addition to the information already outlined the report provides maps on station locations, topography, annual mean precipitation (mm), acid deposition, sulfate, pH, air trajectories, dry and wet deposition.

Effect of Acidic Precipitation on Coniferous Forest

G.Abrahamsen, K.Bjor, R.Horntvedt, B.Tveite

This section summarized the preliminary results of the studies in conifer forests obtained in the first phase (1972-1975) of the SNSF project. The results are based on sampling of the natural precipitation above and below the vegetation canopies, on the application of simulated acid rain to field plots and lysimeters and on regional tree growth surveys. Preliminary results of these studies have been presented in FR 2/75 (Abrahamsen *et al*) while description of the field studies are found in FR 4/76. When published, this report was certainly the most comprehensive, detailed and up to date record of the effect of acid rain on the terrestrial ecosystems.

It was found that the throughfall under the tree crowns was enriched in sulfate, chloride, sodium, potassium, calcium and magnesium. This is due in part to wash-off of dry deposits and foliar leaching. Birch in contrast to pine and spruce, reduced the acidity of the rain. Increasing rain acidity cause increased foliar leaching of calcium, magnesium and other cations.

Increasing the acidity (pH 6.0 to 2.0) of the simulated acid rain in the field plot experiments reduced the pH, the content of exchangeable metal cations and the base saturation in the top (organic) layers of podzol soils. Less podzolized soils were influenced less by acid rain.

The authors state that the lysimeter experiments with a podzol soil revealed that the pH of the leachate was significantly decreased by the simulated acid rain. In the podzol-brown earth lysimeter the pH of the leachate was not influenced. Unfortunately, more soil information such as Fe and Al values is not provided and nowhere do the authors provide a definition of podzol and brown-earth. This information would be useful when referring to Canadian soils' research. Different amounts of water were applied to the two sites, (25 mm/mo on podzol brown earth, 50 mm/mo on podzol) and the vegetation differed as well between the two sites. Net loss of nutrient elements was, with the exception of calcium, much smaller from the podzol-brown earth than from the podzol soil. In the podzol-brown earth lysimeters net losses are found for Ca, Mg and Al. In the podzol lysimeters net losses are additionally found for Mn, Na, K, Fe and in some cases nitrate.

Information in graph form is presented on soil reaction at different soil depths to total amount of acid applied in simulated rain and nutrient budget of podzol and podzol-brown earth lysimeters are related to pH of simulated rain.

The data provided in FR 2/75 for the effect of acid rain on enchytraeids and nitrification were presented here with no significant changes. Consistent effects due to acid rain were not observed. In addition information in graph form is

presented on soil reaction at different soil depths to total amount of acid applied in simulated rain and nutrient budgets of podzol and podzol-brown earth lysimeters as related to pH of simulated rain.

In the acidification experiments on field plots, foliar lesions as necrotic spots were observed on birch (*Betula pubescens* Ehrh.), willow herb (*Chamaenerion angustifolium* (L.) scop) and Scots pine at pH 2 and 2.5 and on mosses at or below pH 3.0.

Experiments with Norway spruce on artificially acidified mineral soil indicate that germination and seedling establishment have a broad optimum within a soil pH range of 4.4 to 5.4; within this range 80% of the seedlings were able to become established, whereas only 20% become established at soil pH 3.8.

The effects of acid precipitation are varied and complex. Negative effects such as increased leaching from soil and decreased bacterial activity may be counteracted by other effects such as increased weathering or fungal activity.

(6) Atmospheric Sulfate Additions and Cation Leaching in a Douglas Fir Ecosystem

D.Cole and D.Johnson; Water Resource Research, Vol. 13, No. 2, 1977, pp.313-317

The authors state that it is the intent of this paper to describe and evaluate the effects of present levels of atmospheric sulfuric acid input on cation leaching at the Thompson Research Center (TRC). The TRC is located in the Cascade Mountains in Washington in a second-growth Douglas Fir-ecosystem.

The study was performed on the Everett soil series (podzolic) a gravelly outwash of glacial origin. Solutions were collected from precipitation, throughfall, beneath the litter layer (4 cm), the base of the A and B horizon (50 cm). The soil solutions were removed by means of a tension lysimeter. Samples were continuously monitored for pH over certain periods of time.

The continuous monitoring of data indicated that precipitation pH frequently fell below 4, but the soil solution never fell below pH 5. Solution pH apparently rose as precipitation passed through the forest canopy and the forest floor. Studies of specific storms showed that most canopy leaching took place during the early part of the storm. Seasonal studies demonstrated that sulfate concentrations in precipitation and throughfall were erratic but generally highest in the late winter and early spring months. Precipitation and throughfall considerations were lowest in fall and winter when heavy rainfall occurred. Sulfate concentrations in forest floor and soil horizons were often unrelated to those of incoming precipitation or throughfall.

In conclusion, the authors state that at present levels, sulphuric acid input via precipitation is smaller in relation to internal cation leaching mechanisms and appears to have its greatest effect on forest canopy leaching. Incoming H^+ is adsorbed and presumably exchanged for cations in the forest canopy and forest floor, so that no effect of acid rain on soil solution pH is detectable. This well designed and thorough study has provided some useful information in the area of pedogenesis and acid precipitation. Similar studies on different soils would also provide information required in order to better understand the effect of acid precipitation on soil environments.

(7) Solution Chemistry of a New Hampshire Subalpine Ecosystem: A Biogeochemical Analysis

C.S. Cronan; *Oikos*, Vol. 34, No. 3, 1980, pp. 272-281.

The author explains that this study in the subalpine zone of Mt. Moosilauke in the White Mountains of New Hampshire was initiated (1) to examine the solution chemistry of the balsam fir subalpine zone in New Hampshire and (2) to evaluate the effect of acidic precipitation on the chemical composition of throughfall, forest floor and soil percolates and ground water in the forest ecosystem. Emphasis in this review will be on the soil results of this study.

The soils of the study area are podzols. Soil solution was sampled as saturated flow with plastic non-tension lysimeters. Most of the lysimeters were placed under the surface organic horizons (12 cm), some beneath the A_2 horizon and a few in the B_2 horizon (25-30 cm).

Cronan found that atmospheric inputs of mineral acids dominated the solution chemistry throughout the soil profile. Sulfate anions supplied 60-90% of the electrical charge balance in the soil leachate. This contrasts with results from soils in unpolluted regions where carbonic and organic acids dominate. It was found that while sulfate and organic ligands dominate the anionic composition of the soil solution, H and Al ions are the major cations in the soil solution. Acidic precipitation caused amorphous and exchangeable soil aluminium to be mobilized and transported in solution through the soil profile and into streams. Cronan states that this modern trend of increased soil aluminum leaching may have implications for pedogenesis, plant community health and the balance of freshwater communities. Potassium, calcium and nitrate are the three ions most strongly retained by biological uptake and/or ion exchange mechanisms in the forest floor and soil profile.

(8) Forest Floor Leaching: Contributions from Mineral, Organic and Carbonic Acids in New Hampshire Subalpine Forests

C.S.Cronan, W.A.Reiners, R.C.Reynolds, G.Lang; Science, Vol. 200, No. 21, April 1978, pp.309-311

In this report the authors present findings from a two year field and laboratory study of the processes which control cation transport from forest floors of ecosystems receiving acid precipitation. Specifically, they compared the relative contribution of carbonic acid, organic acid and precipitation-borne mineral acids to cation replacement and transport processes in the forest floor of a cool, moist, balsam fir, subalpine forest in New England. It was assumed that by measuring the sum totals of major anions of SO_4 , NO_3 , HCO_3 and Cl and major cations (Ca, Mg, K, Na, H, NH_4 , Al, Fe, Mn) one can indirectly estimate the organic anion concentration and evaluate the relative contribution of different acid anions in maintaining electrical neutrality. Both soil solutions and groundwater seepage were collected within 1 week of major rain events, placed in polyethylene bottles and analyzed for pH within several hours of collection, then stored at 4°C in the dark or frozen.

Results indicated that sulfate anions supply 76% of the electrical charge balance in the leaching solution. This result implies that atmospheric inputs of sulfuric acid provide the dominant source of both H^+ for cation replacement and mobile anions for cation transport in subalpine soils affected by acid precipitation. In soil of relatively unpolluted regions, carbonic and organic acid dominate the leaching processes.

(9) Aluminum Leaching Response to Acid Precipitation: Effects on High Elevation Watersheds in the Northeast

C.S.Cronan, C.L.Schofield; Science, Vol. 204, 1979, pp.304-306

The authors present summary data illustrating the unexpected importance of dissolved aluminum in the solution chemistry of ground and surface waters from high-elevation watersheds exposed to regional acid precipitation. Next they discuss the effects of increased aluminum leaching upon pedogenic processes, watershed biogeochemical processes and fish populations inhabiting acidified aquatic systems.

In a New Hampshire balsam fir forest water samples were collected in four strata: bulk precipitation, canopy throughfall, forest floor and A_2 horizon percolate, and spring seeps. In the Adirondack Mountain Lake district surface

water chemistry was characterized.

In a New Hampshire forest it was found that H_2SO_4 was prominent in the precipitation and leaching of aluminum was pronounced in the soil profile. Al is derived from rock weathering and has a pH dependent solubility. In most podzols, Al concentrates in the B horizon. The balsam fir zone of the U.S. northeast presents an interesting contrast as dissolved Al is reaching high concentrations in the forest floor and continues to increase with soil depth. Thus, although organic ligands may be inducing some cation transport it appears that the high concentration of dissolved Al through the soil profile may be accounted for by the low pH of the H_2SO_4 dominated soil solution.

The limnological studies in the Adirondack Lakes indicated that much of the soil-derived aluminum may be transported from the surrounding watershed to acidified lakes. Al contents of acidified lakes are 10-50 times higher than concentrations in circumneutral waters from the same region.

The increased transport of Al to aquatic systems may indirectly affect phosphorus availability through increased inorganic precipitation of aluminum phosphates and clay mineralogy.

(10) The Nature, Distribution and Effects Upon Vegetation of Atmospheric Impurities In and Near an Industrial Town

C.Crowther and A.G.Ruston; The Journal of Agricultural Science, Vol. 4, 1911-1912, pp.25-55

In what very easily may be the first study of acidic precipitation, rain samples were analyzed from Garforth and Leeds, England (1906-1910). The effect of atmospheric impurities on vegetation and soils were also investigated. The vegetation findings will be presented in another section of this bibliography.

Evaluating the composition of rainfall was the major emphasis of this study. To this end the N, S, Cl and free acidity of rain samples were determined. The detailed results will not be discussed in this review but are presented in the paper itself. At Leeds, which is located on the northeastern fringe of the Yorkshire coalfield, total suspended matter, ash, tar, soot and the chemical elements previously outlined were determined in the rain samples.

An experiment with Timothy grass involved the determination of the effects to soil and vegetation caused by the systematic application of waters acidified with H_2SO_4 . Boxes were filled with soil from a "well-mixed heap" watered with 1, 2, 4, 8, 16, and 32 parts of H_2SO_4 per 100,000 neutralized Garforth rain and Leeds rainwater. Unfortunately the term "soil from a well-mixed heap" does not divulge

much information about the soil, ie., is it acidic, sandy, rich in humus, etc? It is in fact interesting to note how similar this laboratory simulation study is to the research being conducted today.

After three years the soils in the boxes underwent chemical and biological examination. Total N, nitrates, phosphoric acid, potash, total carbonate and absorptive power for oxygen data were obtained.

Increasing acidity led to decreasing contents of nitrites and carbonated absorptive power for oxygen. Ammonia content increased as did unspecified easily soluble mineral ingredients. Leeds rain had the same effect on the soil as the 1 part per 100,000 (pH 3.0) solution.

The total number of bacteria diminished rapidly with increasing acidity. Although there are many inadequacies in such areas as sampling design, soil identification, etc. the fact to be stressed is that in the early 1900's acidic precipitation was common in Industrial areas of England and research of a similar nature to that in progress today was being conducted.

(II) The Effects of Acid Rain on Nitrogen Fixation in Western Washington Coniferous Forests

R. Denison, B. Caldwell, B. Bormann, L. Eldred, C. Swanberg and S. Anderson; Water, Air, and Soil Pollution, Vol. 8, 1977, pp. 21-34

Since N is a major limiting factor in Northwestern coniferous forests a decrease in N_2 -fixation brought about by acidic precipitation could seriously affect the forest ecosystem.

Initially a study of the rainfall in three forests demonstrated that the rain pH is no longer under carbonic acid control. The authors then attempted to simulate the effects of acid rain on soil using H_2SO_4 in the laboratory. Soil was placed in Buchner funnels and rain of pH 3 (H_2SO_4) was added to the soil at the rate of 0.5 $cm h^{-1}$. The results of this experiment were highly variable. After 4-8 hours the pH of the leachate had dropped. However, the leachate pH of the second simulated acid rain application a few days later was nearly as high as the first application.

In another experiment soil plots were constructed by sinking cylinders 30 cm in diameter into the soil to a depth of 10 to 15 cm. One plot was untreated, the other four received 5.12 l. of pH 6.0, 5.0, 4.0 and 3.0, H_2SO_4 and water. The water was prepared from tap water not distilled water. The tap water was never analyzed and may have contained appreciable amounts of bases and metals. In this experiment there was no detectable N_2 -fixation in most of the soil samples. The authors added 15 cm of "rainfall" and analyzed the soil immediately. If more water

had been added to the soil and a longer time period used some changes may have occurred in the soil.

The authors conclude that the low rate of N_2 -fixation in soil and litter is probably due to naturally acid conditions not acidic precipitation. Buffering by the canopy, litter and soil may protect microorganisms from the effects of acidic precipitation in this area. One assumes from the title of this paper that the research was conducted in the forests of Western Washington when in fact the majority of soil work was done in the laboratory in a short period of time. In the conclusions the authors should stress the fact that they are projecting a few experimental findings to the field where other factors such as time, amount of rainfall, etc., may vary the N_2 -fixation in nature.

(12) Aluminum Chemistry in Acid Sulphate Soils

C.R. Frink; In: Acid Sulphate Soils, Proc. of Int. Symposium on Acid Sulphate Soils, 13-20 August, 1972, Netherlands Wageningen Pub. No. 18. Vol. 1, pp. 131-167

Many of the properties of acid soils are controlled by the chemistry of aluminum. Hydrolysis of the aluminum ion produces a moderately strong acidic environment. This paper does not deal directly with acidic precipitation and its effect on aluminum in soil. It is strictly a pedological review of aluminum chemistry in sulphate soils. However, the reaction of aluminum in an acidic soil environment tends to be the same whether the initial release of aluminum is triggered by acidic precipitation or natural weathering.

Frink begins by considering the reactions of aluminum in aqueous solutions and then examines how these reactions may be modified in clay suspensions. The chemistry of aluminum in soils is then examined; and finally Frink considers the effects of aluminum on the physical properties of clays and soils.

Both solid phase and soluble aluminum species may be adsorbed by expanding layer silicates. As a result cation exchange capacity is reduced and lattice expansion and collapse is considerably restricted. In addition, aluminum reacts with clays, causing increased aggregation, viscosity and tensile strength but reduces macroscopic swelling. Although iron has long been thought to be the principal cementing agent in soils, it now appears that aluminum is of major importance in creating structural stability. However, an explanation of aluminum behaviour is difficult because of the uncertainties about both the nature of the solid phase and monomeric and polynuclear dissolved species.

This introductory literature review includes a bibliography of over 100 papers on aluminum chemistry in relation to soil acidity.

(13) Potential Effects of Acid Precipitation on Soils in the Humid Temperate Zone
 C.R.Frink, G.K.Voight; Water, Air and Soil Pollution, Vol. 7, 1977, pp.371-378

The purpose of this paper is to examine the potential effects of acid precipitation on soil and to relate these effects to acidification resulting from natural pedogenic processes or from modification of these processes by agricultural practises.

Prior to the presentation of the results from lysimeter studies in Connecticut is a discussion of the soil sulphur and nitrogen cycles and an excellent, thorough review of soil acidity.

The authors state that the direct effects of the H^+ ion in precipitation will be modest in soil. As an example, the acidity in 114 cm rainfall/yr with a pH 4.3 would require 28.5 k/ha of limestone for neutralization. Agronomic practise in Connecticut frequently dictates limestone addition as high as several thousand kg/ha to neutralize acidity generated by a combination of natural processes and fertilizer amendments. In a 10 year (1931-1940) lysimeter study in Connecticut, in which tobacco was grown, soil pH decreased from 5.4 to 5.0. Sodium was not readily retained and was leached almost completely. Magnesium also appeared to leach readily, with a slight release from soil minerals possible. Calcium, however, was leached in amounts much greater than those added, and soil minerals were obviously decomposed. From 40-50% of the added K was fixed in these soils and was not lost by leaching. Thus it appears that changes in unmanaged soils induced by acid precipitation alone will be modest and subtle and probably cannot be expressed completely by measuring changes in soil pH values. The data from a 1930's study of forest soil reveal that in the absence of roots, large amounts of nitrogen and other elements are lost by leaching. In the presence of roots, however, the amounts are very low, and were less than the amounts added in rain. Hence, plant nutrients in rain are apparently taken up at least in part by vegetation and are an important part of the nutrient budget of forest stands.

At present, according to the authors, acid precipitation does not appear to pose a serious threat to soils in the northeastern U.S.A. It should be emphasized, however, that Frink and Voight based their conclusions on research that had been conducted by others in the 1930's.

(14) Predicting Potential Impacts of Acid Rain on Elemental Cycling in a Southern Appalachian Deciduous Forest at Ceweeta
 B. Haines and J. Waide; In: Effects of Acid Precipitation on the Terrestrial Ecosystem, T. Hutchinson and M. Havas (eds.), Plenum Press 1980, pp. 335-340

The authors explain that chronic exposure of ecosystems to acid rain has a

potential to disrupt the cycling of plant nutrients upon which continued plant productivity in part depends. Understanding the magnitude and consequences of this disruptive effect is critical to the development of alternative ecosystem management strategies. Work is being conducted on an experimental watershed in North Carolina, U.S.A. The main features of the investigation are briefly described for the interests of others who plan to do related investigations.

Work in progress is designed to test the following null hypotheses: 1) loss of ions from leaves is independent of rainfall pH over the range pH 5.5 to 5; 2) if the rain pH does affect the amount of elements leached per unit leaf area, the rates will be the same for all dominant tree species; 3) kinetics of ion uptake by roots are independent of hydrogen ion activity over the range pH 5.5-3.5; 4) if the kinetics are affected by pH, roots of all dominant species will behave the same; 5) nutrient loss from forest soils are independent of the pH of extraction solutions (pH 5.5-3.5); and 6) if nutrient loss occurs, the curves of nutrient recharge of soil exchange sites are the inverse of the leaching curves. Many studies fail to report hypotheses or perhaps never do establish them. The hypotheses in this research project are simple, clear and presented prior to the research methodology and results.

Seedling leaves are leached with simulated rainfall (SO_4 , NO_3 , Cl at 10:7:1) for 1 hour per week at the rate of 0.89 cm/hr. The rain is acidified to pH 5.5, 4.5, 3.5 and 2.5.

Soil leaching studies have been performed on aliquots of a statistically representative composite sample from the forested watershed. Although not described in any more detail one assumes that the appropriate horizons of a number of profiles in the area were amalgamated and placed in a lysimeter-type holder. By this method the soil structure would be destroyed and the soil does not represent that typical of the surrounding environment. It is the reviewer's opinion that data from a number of undisturbed profiles from the area would be more valuable. This soil was leached at pH 5.5, 4.5 and 3.5 with a number of different salt solutions. Samples were also agitated on a shaker for 20 hours.

In an attempt to quantify effects of H^+ on elemental uptake by tree roots, isolated roots from seedlings growing in pots and irrigated with experimental solutions have been studied. Solution samples from leaves, soil and root experiments are analyzed for Na, K, Ca, Mg, SO_4 , NO_3 and C (no precise methods given).

It is hoped that integration of the experimental work with ecosystem models will make possible predictive simulation of long-term response to acid precipitation. At this time there are few modelling predictive-type papers concerned with acid precipitation. Although the authors have not developed

models for acid precipitation the results look promising and have practical applications.

(15) Sulfate Mobility in an Outwash Soil in Western Washington

D.W. Johnson, D.W. Cole; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 489-495

The effect of acidic precipitation on cation leaching in a second-growth Douglas fir ecosystem at the Thompson Research Center is reviewed. A lysimeter study plot was leached with aliquots of H_2SO_4 ranging in concentration from 10 to 1000 times higher than natural rainfall and a number of soil sulfate adsorption studies were conducted in the laboratory. Incoming precipitation was shielded from the plot during the application. Solution samples were taken daily following the application and analyzed for pH, specific conductivity, HCO_3^- , SO_4^{2-} , cations and Mn^{2+} .

Sulfate at high concentration proved to be immobilized, presumably by adsorption to soil sesquioxide surfaces. Soil sulfate adsorption was determined at varying sulfate concentrations and two mechanisms of adsorption were implied by the shape of the isotherms.

The authors stress that when considering the effects of acidic precipitation on cation removal from a given ecosystem the mobility of sulfate in the given soil must be considered, or there exists a distinct possibility of overestimating the net transfer of cations due to acid deposition. The data presented here show that the ecosystem studied has the ability to buffer and moderate cation losses due to heavy loads of H_2SO_4 over short periods. Sulfate interacts strongly with soils that have appreciable sesquioxide contents, and the characteristics of this interaction must be known and employed in evaluating the modelling cation losses due to H_2SO_4 deposition.

(16) Acid Precipitation and Soil Sulfate Adsorption Properties in a Tropical and in a Temperate Forest Soil

D.W. Johnson, D.W. Cole, S.G. Gessel; Biotropica, Vol. II, No. 1, 1979, pp. 38-42

The input and leaching of H_2SO_4 in a tropical and temperate forest were compared and related to soil sulfate adsorption properties. Most H^+ was removed from the incoming solution in the forest canopy, allowing a pH rise and bicarbonate domination of the soil solution anion component. Yearly SO_4^{2-} budgets indicated that the tropical site was accumulating SO_4^{2-} whereas the temperate site was in a

near steady state. Laboratory studies showed that the tropical soil had a much greater SO_4 adsorption capacity than the temperate soil, which is probably due to the higher sesquioxide content in the former. The authors hypothesis that the tropical soil is resistant to SO_4 leaching because of its high sesquioxide content.

Different techniques for determining SO_4 content of the soil were used at each site. This might make comparisons between the two sites meaningless. The paper also provides information from precipitation and throughfall research for both temperate and tropical areas.

(17) Effects of Sulphuric Acid Rain on Two Model Hardwood Forests

J.J. Lee and D.E. Weber; EPA-600/3-80-014, January, 1980, 39 pp.

Simulated sulfuric acid rain (cations and anions added) was applied to two model forests (sugar maple and red alder). Data from soil leachate collected at 20 cm and 1 m will be presented here while the throughflow research will be discussed in another part of the bibliography.

Each of 18 lysimeters with reconstituted soil received simulated rain at one of four acidities; 5.6, 4.0, 3.5 and 3.0. From June 1976 to August 1979 water samples were collected from 20 cm and 1 m depth below the surface of the soil. The experimental procedures are well documented and described in detail in the report.

For the first 6 months there were no apparent differences in SO_4 , Mg or Ca concentrations in the soil solution at 20 cm from plots receiving acid or control treatments. After this time SO_4 concentrations on plots receiving "rain" at pH 3.0 became increasingly higher until after 3 years they were equal to SO_4 concentrations in the rain. Soil solutions with pH 3.5 and pH 4.0 treatments responded similarly, 1 year and 2 years, respectively, after the experiment began. Increased Ca and Mg concentrations and decreasing pH at 20 cm in the soil occurred with increasing SO_4 concentration. However, at 1 m in the soil no acid rain related effects were evident after 3.5 years.

These data were then compared to theoretical predictions using the LEACH computer model which simulates the response of soil solution chemistry to acid rain. According to the LEACH simulations, the changes in soil solution chemistry (increased Ca and Mg concentrations, lower pH) were almost due entirely to increases in total anion concentration rather than to change in base saturation. SO_4 concentration in the 20 cm soil solution increased considerably faster than predicted by using laboratory findings in a Langmuir representation of SO_4 absorption.

(18) Acid Precipitation: Chemical Changes in the Soil
N. Malmer; Ambio, Vol. 5, No. 5-6, 1976, pp. 231-234

This article deals with the chemical effects arising in the soils as a result of the acidification of the precipitation, especially in relation to conditions in the Scandinavian countries.

The paper opens with a definition of soil and an overview of soil type, soil acidity and soil formation processes is presented. There are many scant and often imperfect explanations of soil processes offered in this introduction. Malmer states that "chemical and physical properties differ widely between different (soil) horizons" which is not always the case. He points out that podzols and brown earths have a characteristic appearance but he does not continue and discuss what these characteristic attributes are. Next, Malmer inadvertently combines two separate theoretical approaches to soil genesis. The "historical" approach to pedogenesis states that soils evolve continuously through time and can ultimately reach a mature state. According to the "systems" approach to soil formation, soil is an open system which may reach a "steady state" of equilibrium with environmental factors. Malmer combines the two theses and states "all soil properties seem to reach a state of equilibrium in relation to the time factor" (231) and "the soil is often characterized as mature" (232). The result is a section of inaccurate information.

Next, Malmer describes "Human Activity" and its effect on soil, especially through changing forest vegetation, and climate ie. acidic precipitation. It is strongly emphasized that "it is a question of proportion and time required rather than whether any effects appear or not", a phrase that is reiterated throughout the Scandinavian work.

In the section entitled "Changes in Soil Acidity" the viability of resampling earlier soil investigations is discussed. The author feels that it is hardly ever possible to resample accurately due to lack of information from the past on sampling site locations, techniques employed, etc. He feels Wiklander's (1973-74) research is dubious. Malmer next describes some experiments using simulated acid rain and is not surprised that everyone finds pH decreases as does base saturation. He stresses that the amounts of acid used in experiments are usually greater than what are found in nature and the time period of experimentation is shorter.

When discussing "Loading Effects" Malmer finds Overrein's (1972) lysimeter work in agreement with Tamm, Wiklander and Popovic (1977) where they all found increased leaching of metallic cations with decreasing pH. However, Malmer also feels that results of lysimeter experiments as regards leaching of minerals are also dubious. The combined nutrient pool of soil and plant is very

extensive compared with the amounts of elements supplied and leached during short periods. In this section (233) Malmer states that increased leaching (of minerals) as a result of acid precipitation is indicated in studies on inland waters. Later on in the paper he seemingly contradicts himself by stating "any general connection between the acidification of lakes and soils is not to be expected because acid water will drain down root channels, stone surfaces and bedrock without having any close contact with most soil particles".

Malmer concludes the paper by stating that our knowledge about chemical changes brought about in the soils due to acid precipitation is far from complete due to the short amount of time that has elapsed since the problem was first recognized and its scientific complexity.

Although there is no new or original research presented by Malmer in this paper, it does provide a comprehensive review of the Scandinavian literature on acid precipitation and soils at this time (1976). The introduction to soils and pedogenesis, however, is often confusing, vague and erroneous.

(19) Effect of Simulated "Acid Rain" on Juvenile Characteristics of Aleppo Pine
(*Pinus Halepensis* Mill.)

D.Matziris and G.Nakos; Forest Ecology and Management, Vol. 1, 1978, pp.267-272

The objective of this study was to determine the effect of simulated "acid rain" on growth and other characteristics of Aleppo pine and to investigate intraspecific variability, which may exist. The vegetation results of the experiment are summarized in another section of this bibliography. The effect of "acid rain" on some soil properties was also investigated and will be reviewed here.

In 1975 seed was sown in pots filled with a mixture of 1:1:1 of a calcareous soil, sand and manure. The percent calcite and dolomite unfortunately are not given. Manure is not to be considered a constituent of soil, therefore, in the strict sense of the word, "soil" as such was not analyzed. The seedlings and the soil were irrigated with rain at pH 3.1 and 3.5 (H_2SO_4 added to deionized water) about 100 mm of simulated acid rain was applied monthly for over a year.

A significant reduction in soil $CaCO_3$ was found at the end of the experiment (8.6% control, 5.6% pH 3.1). The authors state that the amounts of Ca, Mg and K had slightly decreased with increasing acidity. However the decrease in Ca was only 17 meq/100 (pH 3.1) from 18 meq/100 (control 5.1), with the changes in Mg and K being even less. Random error could account for these changes. The pH of the original "soil-manure" mixture was 7.4 and it did not change with application of "acid rain", a fact the authors failed to mention.

(20) Acidity of Precipitation as Influenced by the Filtering of Atmospheric Sulphur and Nitrogen Compounds - Its Role in the Element Balance and Effect on Soil
R.Mayer and B.Ulrich; Water, Air and Soil Pollution, Vol. 7, 1977, pp.409-416

Data are presented based upon an element balance investigation in a beech forest in Central Germany. It may be considered as a clean air region by Central European standards.

The study includes analysis of rain, stemflow, throughflow, litter and soil. The investigation results are presented in the appropriate section of the bibliography while the soil findings are described here.

In a calcareous soil nearly all the H^+ ions were neutralized. The acid soil neutralized more than 80% of the added acidity, likely due to Al buffering. The buffering of the soil solution takes place in the upper 20 to 30 cm of the soil, most accentuated in the uppermost 1 to 2 cm of the mineral soil (one assumes this means upper B horizon and not the organic rich A horizons). Here pH values as low as 3 are observed.

The buffering of protons and the accumulation of Fe is balanced by the loss of Al, Mn and to a smaller extent Na, K, Ca and Mg. The authors feel this is due to the weathering of silicates and/or desorption from the exchangeable fraction. These processes change the soil chemical conditions in the top of the soil. Tree growth would not be affected by the change but perhaps plant roots could be. The authors calculate that approximately 1% of the total clay and plagioclase will be lost yearly at the present rate of acidification found in this forest.

It is concluded that the acidification of soil and associated loss of Mg may become a problem in the near future.

(21) Acid Precipitation Effects on Soil pH and Base Saturation of Exchange Sites
W.McFee, J.Kelly, R.Beck; Water, Air and Soil Pollution, Vol. 7, 1977, pp.401-408

According to the authors, acid precipitation entering the soil has three possible fates: 1) it may be neutralized by free bases such as $CaCO_3$ and $NaCO_3$; 2) the acid water may pass through into the ground water in soils that are already acid and/or have low C.E.C. ex. sands with low organic matter contents; and 3) the most common situation, acidic ions enter into exchange reactions with cations already present in the soil-cation exchange complex.

The authors calculate that 100 years of precipitation (10,000 cm at pH 4.0) could be expected to shift the base saturation in the top 20 cm of a typical midwestern forest soil (C.E.C. of 20 meq/100 g) downward 20% thus lowering the

pH of the A₁ horizon by approximately 0.6 units, if there are no countering inputs of basic material. Four such countering forces are neutralization by basic substances in the polluting medium itself, nutrient recycling, mineral soil decomposition and exchangeable cations present on negatively charged soil particles.

With fairly well buffered soils, those with moderate amounts of clay or humus, the movement of pH is going to be slow in terms of experimental time, but fast geologically.

(22) Ion Adsorption Isotherms in Predicting Leaching Losses from Soils Due to Increased Inputs of "Hydrogen" Ions - A Case Study

S.I.Nilsson; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.537-552

From a general knowledge of soil science one can formulate hypotheses concerning the impact of decomposition and mineralization processes, dissolution of compounds, soil mineral weathering, ion exchange and leaching. Nilsson feels the following strategy is most optimal in studying the effect of acid precipitation on forest production in Scandinavia: 1) make quantitative predictions concerning changes of acid base variables in the soil; 2) look for significant change in the nitrogen mineralization rate.

To answer the question "does acidification cause a significant change in the equilibrium between soil solution and soil colloids revealed as slope alterations of ion adsorption isotherms?" separate plots in a 22 year old Scots pine stand were treated with 1) 50 kg H₂SO₄ ha/yr once a year from 1970-1976; 2) 100 kg H₂SO₄ ha/yr once a year from 1969-1976; 3) lime applied in 1969 (1960 kg Ca/ha); and 4) irrigation with water from an oligotrophic lake. This is a continuation of the work done by Tamm *et al* at Lisselbo, Sweden (1977).

In 1977 soil samples representing the Ao and at 0-5 and 5-10 cm were collected and analyzed for organic matter content, exchangeable hydrogen ions and base cations. Soil solutions were prepared from chloride salts. The soil samples were equilibrated with the soil solution and from the analysis of cations, H⁺ and original solution adsorption isotherms for Ca²⁺ were obtained.

There was a large spatial heterogeneity in ion exchange properties, judging from comparisons within horizons and between treatments. The answer to the question asking whether acid treatment could alter the potential interval and the isotherm slope appears to be no. A linear multiple regression with organic matter content and median ionic strength values as independent variables and the isotherm

slope as the dependent one explained 89% of the slope variance.

The failure of the model when applied to mineral soil 5-10 cm together with independent data (base saturation) are taken as evidence for the acidification effects being restricted to the upper two soil horizons investigated.

The inclusion of clay fraction data into this "difference model" is discussed. This was not done in the present study which comprises an extremely sandy soil.

The following proposals for further testing are given: 1) investigation along emission gradient with comparable forest and soil types; 2) field experiments using an array of soil types and acid treatments.

Nilsson concluded that the theory of ion adsorption isotherms has potential as an index of susceptibility.

(23) Changes in Chemical Processes in Soils Caused by Acid Precipitation

S.A.Norton; Water, Air and Soil Pollution, Vol. 7, 1977, pp.389-400

This paper examines the changes in the nature of precipitation brought about by acid precipitation and the anticipated change in mineral stability and element mobility in the rock-water chemical system.

According to Norton the acidification of precipitation, primarily rain, causes several significant changes in the characteristics of rainfall, they are: 1) decreased pH; 2) increased H^+ buffering; 3) increased Eh buffering caused by SO_4^{2-} and; 4) increased dissolved solids.

The possible results of this precipitation falling on soil are: 1) increased mobility of most elements. The change in mobility is essentially monovalent, divalent, trivalent; 2) Increased loss of existing clay minerals. However, this may, under certain circumstances, be compensated for by the production of clay minerals which do not have essential alkalies; 3) A change in cation exchange capacity, in some cases an increase, in others a decrease; 4) A general proportionate increase in the rate of removal of all cations from the soil. In initially impoverished or unbuffered soils the removal may be significant in the time scale of 10-100 years; 5) An increased flux of nutrients through ecosystems contiguous with the soil and through aquatic ecosystems "below" the soil zone.

The general result in soil developed on non-carbonate substrates is a tendency toward extensive podzolization, with associated decrease in clay minerals, loss of cation exchange capacity and decrease in fertility. Norton warns that the reestablishment of proper levels of nutrients in the soil may take either artificial fertilization or hundreds of years of chemical weathering and plant activity.

(24) Sulphur Pollution Patterns Observed; Leaching of Calcium in Forest Soil Determined

L.N. Overrein; Ambio, August, 1972, Vol. 1, No. 4, pp. 145-147

This report deals with two aspects of sulphur pollution. First, the deposition pattern around a Norwegian industrial center was charted, and then experiments were conducted to determine the effects of precipitation of varying acidity on the calcium level of forest soils.

A 40 cm deep podzolized forest soil was exposed to 500 mm/mo simulated acid rain (pH 2.0-6.0) in a series of lysimeter investigations. After 40 days a steadily increased leaching of Ca became apparent when water at pH 4.3 was applied to the soil in contrast with the control (distilled water) which showed a low constant rate of leaching.

Leaching of Ca was also studied in soils of different physical and chemical compositions. A sharp increase in Ca leaching occurs in all soils as the pH of the precipitation approaches 4.0. Fine sand demonstrates a more drastic increase in Ca leaching than clay or loam soils.

During the first 20-days of a buffering capacity experiment on a sandy soil the soil showed no significant difference with respect to the pH of the leachings at 40 cm. During the next 60 days the acidity of the leachate gradually increased. Acidification of the ground water coincided with the acidification which took place in the soil profile.

Overrein concludes the report by stating that the ultimate effect of acid precipitation on the soil depends on the amount of acidic precipitation that penetrates the soil, the time period over which the penetration takes place and the neutralizing capability of the soil. Overrein cautions that sulphuric acid causes cumulative damage on soils when precipitated on the ground.

(25) Changes in Soil Productivity Through Acidification. The Norwegian National Research Program "Acid precipitation - Effects On Forest And Fish"

L.N. Overrein; Symposium Session Papers, 11th Congress of Soil Science Vol. 3, 1978, pp. 260-277

Overrein begins this paper with a review of acid precipitation, its sources, chemical composition and spatial distribution. He then discusses soil formation, soil acidity, soil acidification on cultivated soils and uncultivated soils. It is stated that the adverse effects on the terrestrial system are often subtle and difficult to document over the short term. Acute effects of acid precipitation on soils and

vegetation have been clearly identified only under extreme conditions, either experimentally induced or in situations very close to sources of heavy air pollution. The most serious consequence of regional acidification at currently observed levels may be the increased rate of leaching of major elements and trace metals from forest soils and vegetation. However, in unmanaged soils acid precipitation might be expected to show pronounced effects, especially on those soils with a low C.E.C., low organic matter and low clay content. Overrein feels that it is a question of proportion and time required rather than whether any effects appear or not.

(26) Podzolization: Mechanism and Possible Effects of Acid Precipitation

L.Petersen; In: Effects of Acid Precipitation on Terrestrial Ecosystems,

T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.223-238

In this report Petersen considers the mechanism and possible effect of acid precipitation on the podzolization of soils. Podzolization is perhaps the most important soil-forming process in areas of cool, north temperate regions having: 1) an excess of precipitation over evaporation; 2) sandy soils of low buffering capacity; 3) usually overlain by heath or conifer-dominated plant cover. Reaction of these soils is acid, they are relatively low in available plant nutrients, they accumulate surface organic matter characterized by a relatively low degree of decomposition, and they have clear well-differentiated eluvial (Ae) and illuvial (Bf, Bhf) horizons. The translocations are caused by water-soluble organic compounds produced during decomposition of plant residues in the upper soil horizons. These compounds move downwards with leaching water and dissolve iron and aluminum from the inorganic soil constituents by complex action. Mutual precipitation of the metals and organic matter takes place when the negative charge of the organic matter has been reduced to a sufficiently low value that the compounds are no longer soluble. Iron and aluminum cause a partial neutralization of this negative charge.

Acid precipitation may affect the process of podzolization in two ways: 1) since an acid surface soil reaction is a pre-requisite for podzolization, additional increments of acid could start the process at an earlier date on susceptible soils; and 2) additional acid inputs could amplify podzolization by increasing the thickness of the eluvial A horizons and further depleting surface soils of nutrients.

The time required for development of podzol may vary from a few hundred years to several thousand years. Even the shorter period is long as compared with

the period in which observations on the occurrence and effects of acid precipitation have been carried out. Petersen does not expect that it is possible as yet to make direct observations on the effect of acid precipitation on podzol development.

(27) Chemical and Biological Relationships Relevant to the Effect of Acid Rainfall on the Soil-Plant System

J.O.Reuss; Water, Air and Soil Pollution, Vol. 7, 1977, pp.461-478

According to the author, the purpose of this paper is not to support or to contest the validity of the hypothesized adverse ecological effects due to acid rain. Rather, the information and concepts presented here are intended to be useful in the formation of testable hypotheses and to provide a firmer basis for future experiments on the soil-plant system.

The theory of the acidity relationship of the carbon dioxide-bicarbonate equilibrium and its effect on rainfall measurements is provided. The relationship of a cation-anion balance model of acidity in rainfall to plant nutrient uptake processes is also discussed. The excess of anions in rainfall can be an appropriate measure of the capacity of the rainfall to contribute to the acidity of soil systems.

The flux of H^+ ions in the soil systems due to plant uptake processes and S and N cycling is considered. H^+ is produced by oxidation of reduced S and N compounds. Plant uptake processes may result in production of either H^+ or OH^- ions. Fluxes of H^+ from these processes are much greater than rainfall H^+ inputs, complicating measurements and interpretation of rainfall effects. The soil acidifying potential due to the oxidation of the NH_4 rainfall is examined, with the conclusion that acidity from this source is of similar magnitude to direct H^+ inputs common in rainfall.

(28) Simulation of Nutrient Loss From Soils Due to Rainfall Acidity

J.O.Reuss; EPA-600/3-78-053, May 1978, 45pp.

This paper describes a model that calculates ion loss from soils as a function of soil properties and of the composition and distribution of rainfall. The objective of the model is to provide a quantitative system that utilizes established principles of soil chemistry to predict the most likely effect of rainfall acidification on leaching of basic cations from non-calcareous soils. The major limitation of the model is the exclusion of all basic cations except calcium.

The model utilizes the relationship between lime potential and base

saturation, the equilibrium between CO_2 partial pressure and H^+ and HCO_3^- in solution, equilibrium of cations and anions in solution, and sulphate adsorption to predict the distribution of ions between solution and exchangeable bases.

The initial results of the investigation indicate that significant acidification and depletion of bases could occur over a period of few decades if rainfall inputs are consistently acidified to pH 4.0 with sulfuric acid. Soils with a significant capacity to adsorb sulfates will tend to damper the effect of H_2SO_4 induced leaching of basic cations.

A point of interest is that the output of this model confirms that soils well supplied with bases are most susceptible to base loss and that as base saturation and lime potential fall to low levels acid precipitation causes leaching of H^+ and Al^{3+} ions rather than bases. These findings confirm Wiklander's (1973/74, 1980) theory.

(29) Studies of Acid Rain on Soils and Catchments

J.E.Rippon; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.499-524

The paper by Rippon describes the experimental design and some preliminary results of acid rain studies on soil and catchments in England. The results of the catchment studies will be described in the section on acid precipitation and its effect on the aquatic system via soils, while the microorganism information obtained from the pot-scale experiments will be found in the soil and microorganism section.

Undisturbed cores of a podzolic soil were placed in lysimeters. They were watered with distilled H_2O in addition to natural rain for 15 months. At the time the monoliths were taken soil samples were collected for subsequent chemical analyses. In addition to leachate collection at the base of the lysimeters, soil water was also extracted from each horizon using ceramic cup probes. Three times a week 10 mm of simulated acid rain to a total volume of 300 liters rainfall equivalent to approximately 1500 mm per year were added to the soil. Distilled water was used as a control, it had a pH of 5.6. The acid rain is sulfuric acid at pH 3.0.

In addition to lysimeter experiments 50 pots were filled with soil from each horizon used for the lysimeter study. Half the pots received distilled water and the remainder sulfuric acid at pH 3.0. The leachate were collected for analysis at 6 monthly intervals.

Experimental acid waterings of monolith and pot soils suggests some

retention of sulphate in soils. The vertical movement of sulphate through the lysimeters required 60 mm of "rain" for each 100 mm depth of soil, the SO_4^{2-} moving with the water front. In the lysimeters H^+ was neutralized by other cations but in the acid watered pots the higher acidity of leachates suggest that a large part of the H^+ is derived from the soil itself.

(30) Alternative Sources of Acidification of River Water in Norway

I.Rosenqvist; The Science of the Total Environment, Vol. 10, 1978, pp.39-49

The Norwegian SNSF group hypothesized that the increased acidity of Norwegian waters is due to increased amounts of acid air pollutants resulting from the increased burning of fossil fuel. The author, Rosenqvist, argues that the input of hydrogen ions from the precipitation is considerably smaller than the production of hydrogen ions in terrestrial ecosystems. He claims that changes in vegetation and humus, due to changes from agriculture to forestry, are the main reasons for the increased acidity of fresh water.

This paper is a precis of an earlier paper by the author, written in Norwegian entitled: *Surjord-Surt vann (Acid Soil-Acid Water)* Ingenior forlaget A/S Oslo, 1977.

In the introduction Rosenqvist does not deny the existence of acid precipitation but states that the high amount of acid in the coastal area of Norway is mainly due to high precipitation values, not to the specific acidity of the rainwater.

When discussing run-off hydrology and pH, Rosenqvist states that every time a river is in flood, the pH is lowered, even where the flood is caused by unpolluted rain. This may be because the organic humic-rich topsoil will buffer the water on the acid side because it represents ion-exchange systems mainly in the hydronium state. This results in a run-off water of enhanced acidity, independent of the original pH of the rain. The topography of the area, the amount of soil and the permeability and porosity of the soil and the underlying bedrock are important variables in affecting the pH of water courses.

Due to the shallow soil cover in Norway, water from precipitation has a short residence time in the ground before it enters lakes and streams. The acid buffering ion-exchange reactions in the humus are rapid but the neutralization by weathering is slow.

Among the factors which may have caused changes in the pH value of run-off water during the last centuries are timber production and export. An additional point, according to Rosenqvist, is the marked change in agriculture in Norway during the last century. The grasslands have changed into forest or heathland. The

growing trees extract bases from the soil and produce humic acid.

It is concluded that acid run-off in water courses is mainly due to ion-exchange processes in the catchment area and only to a minor degree to the H^+ content of the precipitation.

(31) Effects of Low pH on the Chemical Structure and Reaction of Humic Substances

M.Schnitzer; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.203-222

In this paper the effects of low pH on the chemical structure and reactions of humic substances in the soil are considered. Humic substances are the most widely-distributed and abundant carbon-containing compounds on the earth's surface, and affect all soil reactions to some degree. They must be considered in any studies concerning the effects of anthropogenic acidification of soils. Humic substances are partitioned by acidification, and are composed of humic acid (soluble in dilute alkali but precipitated by acid), fulvic acid (soluble in both alkali and acid) and the relatively unreactive humins (insoluble in both acid and bases).

Several characteristics of acid-soluble fulvic acid which are affected by pH changes include: 1) changes in structure from a stringy, low density material at low pH to a fine-grained, high density, plate-like structure at high pH; 2) a decrease in the electron-spin resonance as pH is raised, which is an estimate of the relative number of free radicals and of molecular size; and 3) changes in the stability constants of fulvic acid-metal complexes which make metals relatively available at low pH's.

Schnitzer noted that he could foresee severe soil degradation under very high inputs of acidic precipitation if large amounts of fulvic acids were to go into solution, with the effect that large quantities of cations could be bound as complexes and lost from the soil system in conjunction with the leaching fulvic acid. A soil pH of 2-3 would be necessary to achieve such a fulvic acid effect on a large scale. Humic acids would not be so affected because they are insoluble at low pH's.

(32) Acid Precipitation and Other Possible Sources for Acidification of Rivers and Lakes

H.Seip and A.Tollan; The Science of the Total Environment, Vol. 10, 1978, pp.253-270

Recently, Rosenqvist stated that although the deposition of acid has increased in recent years, this did not account for any appreciable change in the acidity of the surface water. He suggests that the greater part of acidity is caused by ion exchange processes in an increased mass of raw humus in the catchment areas, an increase related to change in agriculture, cattle management and forestry. This report deals mainly with the evidence for a relationship between acid precipitation and acidification of surface water.

The trends in the recent acidification of rivers and lakes in south Norway are examined and the evidence for a causal relationship between acid precipitation and acidification of surface water is critically reviewed. Results from regional surveys, studies in small catchment areas and from percolation experiments are presented.

The authors found, in both Europe and North America, acid lakes and rivers where the acidity has no obvious source in the drainage basins and areas with both high deposits of acid precipitation with geological conditions which do not favour neutralization of acid and reduced fish population in acid lakes. These findings led the authors to hypothesize that there exists a causal connection between the acid precipitation and acidification of surface waters. The authors do admit that not only the H^+ in precipitation is of importance and that the understanding of the details of the processes in the catchment areas is incomplete.

The authors conclude that although changes in agricultural practices and forestry may contribute to soil acidification and acidification of surface waters in "some" areas, the most affected region in Southern Norway seems to show that such changes cannot be the most important reason for the regional acidification in the studied area.

(33) Sulfur Distribution and Cycling in a Deciduous Forest Watershed

D.S.Shriner, G.S.Henderson; Journal of Environmental Quality, Vol. 7, No. 3, 1978, pp.392-397

Sulfate sulfur concentration and pH of precipitation and streamflow, and sulfur concentration of biomass and soil components, were determined for a 97.5 ha mixed deciduous forest in eastern Tennessee. Sulfate contents of the vegetation

and soil were determined with a Leco analyzer while precipitation samples were analyzed for SO_4 using a Technicon Autoanalyzer and a methylthymol blue procedure. Amounts of S added by precipitation and lost by stream flow were compared to fluxes of S between biomass pools. Of the 6.6 kg/ha per year accumulation of S for the watershed as a whole, 8.6 kg accrue to mineral soil while 4.3 kg are lost from organic soil horizons and 2.3 kg are due to the annual increment of vegetation.

In the short-term study a net annual loss of S from organic soil horizons was observed. This loss was offset by a net gain in the mineral soil horizons. Approximately 29% of the total pool of S in the organic soil horizon is transferred to the mineral soil each year. Leaching of the organic horizon may be a significant mechanism of transfer to the mineral soil pool.

The behaviour of S on Walker Branch Watershed appears to differ significantly from locations in the northeastern U.S., however, the data show active expansion to the south-eastern U.S. of the area affected by atmospheric sulfate pollution commonly associated with the northeastern region of the U.S.

Although this paper deals more with S pollution rather than acidic precipitation, the information provided through such a biogeochemical study is useful as it can be related to acid precipitation. This type of S information may be applicable when assessing the input of SO_4 on forest production, element cycles and interaction with the aquatic environment as well as providing guidelines for similar studies in regions affected by acid precipitation.

(34) Effect of Simulated Acid Rain on Sulfate Movement in Acid Forest Soils

B.R. Singh, G. Abrahamsen, and A. Stuanes; Soil Sci. Soc. Am. J. Vol. 44, 1980, pp.75-80

This article is part of a series of investigations of the effects of acidic precipitation on the movement, adsorption and desorption of sulfate in acid forest soils. The authors wish to determine the effect of simulated acid rain on sulfate movements and leaching of other nutrients in two Norwegian acid forest soils (semi-podzol and iron podzol).

The study was carried out using lysimeters filled with undisturbed soil. Two pH levels of artificial rainwater (pH 5.6 and pH 4.3) were used. Detailed explanations of materials and methods used are given in the article, including such information as the chemical properties of the soils, the ionic composition of the simulated rain and the type of analyses used.

It was found that the mobility of sulfate and the leaching losses of elements

were higher in the semi-podzol than in the iron podzol. Both the soils were found to accumulate sulfur. This suggested to the authors that in the long-term application of acid rainfall, these soils may not lose cations because specific adsorption of sulfate may cause an increase in cation exchange capacity of these soils, thereby helping them to retain cations.

(35) Geology Controls Acid Rain Input

R.G. Skinner; Geos, winter, 1980, pp. 2-4

Skinner suggests that maps recently produced by the Geological Survey of Canada can aid towards understanding and assessing the current threat of acid precipitation.

In the introduction the author defines acid rain, explains generally what pH means and states that terrestrial ecosystems may be under stress due to acid precipitation. The author states that the clues to the potential susceptibility of a terrain to acid rain rests in the rocks and the mineral debris which serve as parent material for the soils. At this point Skinner seems to have overlooked the role that soils themselves play in buffering, transferring and storing the various components in acid precipitation. Generally the ubiquitous crystalline rocks of the Canadian Shield have little or no buffering capacity. Geological maps however, reveal large areas of calcareous rocks which can neutralize acidity in the rain.

The text of the paper includes a map of lake acidity north of Lake Superior indicating areas of acid prone soils. Map 2 of bedrock units seems to control many of the pH patterns in Map 1 of lake water acidity. Maps of high levels of arsenic, fluorine and mercury in lake waters will reflect the bedrock content of these elements in the natural formations. A better understanding of geology can lead to a better understanding of natural hazards that could be worsened by acid precipitation.

(36) Effects of Acid Precipitation on Soil Leachate Quality: Computer Calculations

G. Sposito, A.L. Page, M.E. Frink; EPA-600/3-80-015, January, 1980, 39 pp.

In order to test the hypothesis that "acid precipitation may interact with Fe and Al hydrous oxides in soil to dissolve these minerals and release the metals they contain into subsurface runoff" a computer program GEOCHEM was employed. This is a chemical thermodynamic model which sets up a mole balance equation for

each component of a soil solution and incorporates thermodynamic equilibrium constants corrected for ionic strength into this equation according to the laws of mass action. A more detailed description of GEOCHEM is included in the paper. Equilibrium speciation in 23 examples of acid precipitation from New Hampshire, New York and Maine and the same number of mixtures of acid precipitation with minerals characteristic of soils in these states were calculated. The speciation calculations on the acid precipitation-soil mineral mixtures demonstrated that Al and Fe amounts in the soil solution were larger than the levels predicted for a soil solution dominated by carbonic acid. The higher levels of soil-bound metals are believed to be caused by the lower pH values in the acidic precipitation and of the presence of metal-complexing ligands. Cation exchangers were found to preferentially adsorb heavy metals (Cd and Pb) which may be found in acidic precipitation.

The authors concluded that percolation of acidic precipitation through the soil tends to dissolve the least stable soil minerals and raise the levels of Al significantly in the subsurface runoff.

One may conclude from this paper that computer modelling appears to provide some useful and perhaps otherwise unattainable information regarding acidic precipitation and its effect on soil. Predictive modelling of this type takes less time than simulated laboratory or field research and will likely be employed more and more by soil scientists to complement former methods of research.

(37) Acid Precipitation: Biological Effects in Soil and on Forest Vegetation

C.O.Tamm; Ambio, Vol.5, #5, 1976, pp.235-238

This paper discusses the possible effect on vegetation and soil organisms of moderate but persisting changes in the "chemical climate" such as the increase in precipitation acidity observed in Scandinavia in recent years. Just the section on "Possible Effect on Biological Processes in the Soil" will be reviewed here.

A number of possible effects due to acid rain on biological processes in the literature are reviewed by Tamm: 1) soil respiration, an expression of soil organism activity, decreased with acidification of humus in a study by Popovic et al (1977); 2) nitrification may be decreased or prevented by soil acidification; 3) ammonification increases rather than decreases in acidified soils; 4) decrease of *Cognettia spagnetorum* occurred in SNSF 1975 studies under acidic conditions; 5) release of Al and heavy metals ions occurs with increasing acidity. These ions may be toxic to many plants.

Tamm presents a hypothetical model on the effects of strong acid deposition

in a forest ecosystem. This model emphasizes the positive and negative feedback mechanisms in the system, which makes forecasting the ultimate result of the atmospheric acidification difficult. Tamm concludes that because some soil processes proved to be sensitive to acidification under experimental conditions that forest ecosystems will likely become less productive and less stable.

Overall the paper provided an adequate review of the literature on soil fertility processes that might be affected by acidic precipitation in Scandinavia. Tamm's hypothetical model also provides a stepping-stone for more detailed and advanced studies on soil and vegetation processes. However, after stressing that no direct proof that acid rain affects forest productivity exists Tamm concludes that Scandinavian forests will become less productive in the long run.

(38) Effects of Application of Sulphuric Acid to Poor Pine Forests

C.O.Tamm, G.Wiklander, B.Popovic; Water, Air and Soil Pollution, Vol. 8, 1977, pp.75-87

In 1969 the Swedish College Of Forestry began field experiments in a pine forest on a glaciofluvial esker 160 km north of Stockholm. These pioneering experiments consisted of leaching field soils with acid and salts. The two parts of the experiment that pertain specifically to soils will be reviewed here. A discussion of the study of pine trees by Tamm will be found in another section.

This paper is a summary of Research Notes, Department of Forest Ecology and Forest Soils, Royal College of Forestry No. 18 Stockholm by C.Tamm, A.Nilsson and G.Wiklander 1974 entitled: The Optimum Nutrition Experiment, Lisselbo. A brief description of an experiment in a young stand of Scots pine.

Lysimeter Experiments - G.Wiklander.

In May 1972, lysimeters were installed at Lisselbo, Sweden. The 40 cm deep lysimeters contained local medium sandy soils with semi-undisturbed ground vegetation and top soil. The lysimeters received 4 treatments: a control (contents unknown), Acid 2 (100 kg H_2SO_4 /ha) and $N_2P_2K_2$ (120 kg N/ha, 40 kg P/ha, 76 kg K/ha) and a combination of these treatments. Natural precipitation was allowed to fall on the lysimeters. The leachate was analyzed at intervals not specified.

The addition of ammonium nitrate had a higher leaching and acidifying effect on the soil than sulphuric acid did. Leaching of H^+ and cations was observed with the second addition of ammonium nitrate. Sulphuric acid did increase the leaching of cations. The calcium loss by adding 100 kg/ha H_2SO_4 was more than for a non-

acid control, but less than for added NPK. The calcium loss from the soil was less than equivalent to the acid added. This is an important comparison because it puts calcium loss by acidification in the context of the wider sphere of soil management.

Soil Incubation Experiments - Popovic

A_0 soil horizons were collected from a number of sites in Sweden then incubated in the laboratory. The release of N was measured in all the soil sampled every 6 to 9 weeks as was the CO_2 evolution in some soil samples. In addition to the incubation experiments, model experiments in the laboratory were carried out with humus samples from untreated areas in the field.

The results from the model experiments were more consistent than the incubation experiments. Incubation studies demonstrate a depression of the release of CO_2 when either H_2SO_4 or powdered S was added, H_2SO_4 being the more effective.

Addition of S usually increased the amount of mineral nitrogen in the samples but lowered the amount of nitrate.

All three authors conclude that acidification of already acid forest soils is a slow process, however, some changes in soil fertility do exist. The authors call for further studies in greater detail on more sites.

(39) Leaching Rate of Heavy Metal Ions in Forest Soil

G.Tyler; Water, Air and Soil Pollution, Vol. 9, 1978, pp.137-148

The leachability of Mn, Zn, Cd, N, V, Cu, Cr and Pb was studied in two purely organic spruce forest soils, one control soil and one similar soil heavily polluted by Ca and Zn from a brass foundry in southern Sweden. Artificial rainwater, prepared in distilled, deionized water was composed to resemble the composition of the rainwater of southern Sweden and acidified with H_2SO_4 to pH 4.2, 3.2 and 2.4. Two liters was added to the soil every day. Percolation of 90% of this volume was completed within two hours. The percolate was sampled for pH and metal ion analyses after a volume of 4, 8, 14, 24, 37, 55, 75, 103 and 125 liters had passed through the leaching bed.

The 10% residence time estimated from the experimental data varied from 3 years (Mn) to 70 to 90 years (Pb) in the control soils and from 2 years (V) to 200 years (Pb) in the polluted soil with a precipitation water of pH 4.2 residence times for most elements studied (except V and Cr) decreased with pH of precipitation water.

(40) Chemical Changes Due to Acid Precipitation in a Loess-Derived Soil in Central Europe

B. Ulrich, R. Mayer, P. K. Khanna; Soil Science, Vol. 130, No. 4, 1980, pp.193-199

The authors studied the effect of acidic precipitation on soil chemistry and ion flux in a stand of Fagus silvatica in Germany between 1966 and 1979. The soil corresponds to a typic dystrochrept with loess as the parent material.

Water samples were collected monthly from open rain collectors, canopy throughfall, stem flow, soil organic layers and in the root zone. H, Na, K, Mg, Ca, Al, Mn, Fe, NH_4 , NO_3 , Cl, SO_4 and PO_4 were analytically determined. Soil was sampled in 1966, 1973 and 1979 with a borer at 10 cm intervals to 50 cm.

Aluminum and organic matter increased in the soil solution and forest floor respectively. The authors hypothesize that acidic precipitation has induced production of internal H^+ ions in the soil through an accumulation of organic matter poor in nitrogen and by a change in the type of nitrogen nutrition. Two-thirds of the H^+ ion buffering is due to the dissolution of polymeric hydroxoaluminium.

An abundance of data is presented in this paper. Often it is difficult to follow the tables because there is so much information and it has been manipulated statistically. A number of sentences are poorly written and awkward which adds to the confusion of the vast amount of information presented. In the conclusion of the report the authors precisely explain what they have found out but they offer no explanation for the theories they present referring to silicate weathering and Al production.

The authors conclude that the forest investigated may be highly endangered by soil acidification caused by acid rain.

(41) The Role of Neutral Salts in the Ion Exchange Between Acid Precipitation and Soil

L. Wiklander; Geoderma, Vol. 4, 1975, pp. 93-105

Neutral salts decrease the pH of the drainage water but reduce acidification of the soil. The effect, termed "salt effect", is a consequence of the competition between H_3O^+ and the salt cations for the negatively charged surfaces of the soil particles.

The magnitude of the salt effect depends on the relative bonding energy of H_3O^+ and of Ca, Mg, Na, K, NH_4 in the soil, as well as the concentration of H_3O^+

and the above cations in the precipitation. The salt effect may be considerable in very acid soils. It decreases with rising pH to become very small or negligible in neutral soils due to the increasing bond energy of H_3O^+ .

Wiklander set up an experiment to study the salt effect as registered by the exchange acidity by the measurement of pH in various soils. Salt solutions containing quantities of Ca, Mg, Na and K, corresponding approximately to the composition of rain and distilled water, all with pH 7.0, were added to various horizons of podzols and brown earth soils. The soil suspensions were shaken overnight and pH measured in the supernatant solution after 3 hours of sedimentation. The results of this experiment indicated that exchange acidity is small in clay soils and increases with decreasing pH of the soil, reaching its highest values in the podzols.

In another experiment a podzol was leached with a H_2SO_4 solution of pH 3.56 from below, at 6 ml/cm² per hour. The experiment included treatments with H_2SO_4 and neutral salts as well as salt solutions without H_2SO_4 . It was found that salts in the percolating solution caused a decrease in pH in the leachate indicating replacement of H and Al from the soil and a decrease of the net loss of Ca and Mg. The salt effect was higher in the B₂ than in the A horizon, reducing the net loss of base cations. This may be explained by the higher C.E.C. of the former, leading to a stronger cation exchange. The analyses also showed that the release of Al and Fe was about the same in the series with H_2SO_4 and salts as in the series with only salts, indicating cation exchange is the principle active instrument.

The experimental results show that neutral salts, added to a soil-water suspension or percolated as dilute solution through soil columns, lead to a cation exchange manifested by a pH drop of the soil solution, termed exchange acidity, and by a corresponding adsorption of salt cations. The net result is an increase in the base saturation of the soil.

The adverse effect of acid precipitation is likely to be less in very acid soils, such as podzols, than in slightly acid and neutral soils with low buffering capacity against pH change. The cations from the salt replace part of the exchangeable H and Al and thereby increase the base saturation of the soil proportionally to the magnitude of the exchange acidity.

(42) Interaction Between Cations and Anions Influencing Adsorption and Leaching
 L.Wiklander; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
 T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.239-254

This paper deals with cation-anion adsorption and mobility. The soil has

amphoteric properties and therefore has the capacity of adsorption and exchange for both cations and anions. The capacity of soils to adsorb and retain anions increases with increasing pH, with the salt concentrations and with contents of hydrated oxides of Fe and Al.

Experiments with both equilibrium and dynamic systems of soils and various salts have shown that certain polyvalent anions of soluble salts added to soils increase the adsorption and decrease the leaching of anions. Thus the solubility and retention of nutrient cations in the soils were determined partly by the associated anions. In experimental work, the effectiveness of the anions studied proved to be: Cl^- , NO_3^- , SO_4^{2-} , H_2PO_4^- , HPO_4^{2-}

The polyvalent anions are bound by hydrated oxides of Al and Fe or by other minerals leaving free negative charges attracting and adsorbing cations. For the experiment different soil types were used: Cambisols (cultivated, loam-loamy clay), a Humo-orthic podzol and a Latosol (lateritic clay). Salt cations used were Na, K, Mg, Ca and Cu. The difference in C.E.C. between phosphate and chloride systems increased for the soils as follows: Cambisol, Podzol B₂, Latosol

When a solution of Ca, Mg, K, Na, H_2PO_4^- was added to a Podzol B₂ soil only Na was leached. The total leaching in the H_2PO_4^- system was 23% of added cations whereas the corresponding figure from the Cl system was 62%. Analysis of soil columns showed a distribution of retained H_2PO_4^- similar to that of the retained Ca, Mg, K indicating the adsorbed phosphate was the active group for holding cations.

Wiklander concluded that we may improve the capacity of soils to adsorb cations and reduce the leaching of cations and anions by using more phosphate as fertilizers. To a lesser extent, sulfate inputs may also be useful in this respect.

(43) Short-Term Effect of a Simulated Acid Rain Upon the Growth and Nutrient Relations of *Pinus Strobus*, L.

T.Wood and F.H.Bormann; Water, Air and Soil Pollution, Vol. 7, 1977, pp.479-488

On October 18, 1973, each of 125 three-inch plastic pots containing 180 ± 6 g

of sandy loam soil were planted with four white pine seeds. Once a week artificial acid rain (pH 5.6, 4.1, 3.3, 3.0, 2.3) was applied to the pots for 20 weeks. Four pots from each subset of 25 were randomly selected for soil leachate analysis. K, Mg and Ca concentrations, pH and N were determined every other treatment.

Marked soil pH declines were measured after 20 weeks of treatment with pH 2.3. Leaching of Mg and Ca steadily increased with "rain" acidity through the pH range 5.6-2.3. K losses did not increase until the "rain" pH was lowered to 3.0 and 2.3. Declines in exchangeable K, Mg and Ca were measured at pH's 3.0 and below. Greatly depleted levels of exchangeable cations were found at pH 2.3.

B. SOIL SUSCEPTIBILITY TO ACIDIC PRECIPITATION

This section is a review of papers which presents information on certain types of soils and how they are affected by acidic precipitation. Data on specific chemical and physical attributes of the soil which determine its susceptibility to change when in contact with acidic precipitation are also presented. Agricultural soils may not be significantly affected at all. Factors such as the soil cation exchange capacity, pH, organic matter content, particle-size, clay type, carbonate content, base saturation and structure all play a role in determining how a soil will react with acidic precipitation. Wiklander, the author of the most quoted theory of soil sensitivity to acidic precipitation, feels that little or no change would be expected on calcareous, well-buffered soils with a pH over 6 or on acidic, moderately buffered soils below pH 5. Soils that are poorly buffered with a pH range of 4-6 are relatively susceptible. Clay soils buffer well and are moderately sensitive.

(1) The Sensitivity of Soils To Acidification

B.Bache; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds.), 1980, pp.569-572

Bache explains that the sensitivity of a site can be considered as the change produced in some property as a result of an applied stimulus. In this paper the soil is being considered as a site and change in its "acid-base status" is being looked for in response to acidic precipitation. The acid-base status is represented by the degree of base saturation (content of exchangeable bases as a percentage of cation exchange capacity). The degree of base saturation is also reflected in the soil solution particularly by the lime potential ($LP = pH - 1/2 p(Ca, Mg)$).

Bache provides three indicators of sensitivity of soil to acidification: 1) The difference in lime potential (change in $LP = LP_{soil} - LP_{water}$). Where this is large the change will be large. Bache expects the greatest change on neutral soils; 2) The buffer capacity of the soil profile. Change in soil acidity is inversely related to buffer capacity, being greatest in poorly buffered soil. In general, soil buffer capacity is lowest in sandy soil and those with low organic matter contents. According to Bache this soil will change most rapidly; 3) The fraction of the water body that reacts with the soil (f_w). Intensity of rainfall, structure of soil, and soil texture, all affect flow of water through the soil.

Bache explains that these principles make it possible to identify sensitive

soils in a semi-quantitative manner. Bache's theories are similar to Wiklander's (1973/74) and he stresses that slightly-acid, poorly buffered shallow soils should be carefully monitored for the effects of acid precipitation.

This paper and McFee (1979) are the only two attempts to provide quantitative formulation for determining soils sensitive to acid precipitation to date. The lime potential would be the easiest of the three factors to measure in soils. Unfortunately there does not seem to be any standardized method to determine f_w . Although the concept of determining the fraction of water that reacts with the soil is useful in studying soils and acid precipitation, in practise determining this factor would be impractical.

(2) Site Susceptibility to Leaching by H_2SO_4 in Acid Rainfall

D.W. Johnson; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds.,), Plenum Press, New York, 1980, pp. 525-535

This paper deals with the various aspects of site sensitivity to acid sulfate loadings. Johnson explains that anion mobility in the soil is useful in assessing soil leaching due to acid rainfall. Total ionic leaching can, therefore, be described by anion flux alone. The aim of this paper is to discuss the factors affecting sulfate mobility in soils in relation to soil properties and site susceptibility.

The major mechanisms of sulphate adsorption in soils were presented and soil properties in relation to sulphate adsorption and susceptibility to leaching by H_2SO_4 were noted. Data from research in the U.S.A., West Germany and Costa Rica were presented.

It appeared that S accumulation was greatest in the most highly weathered soils. These soils should not be susceptible to detrimental effects from acid sulphate loadings since the sulphate would not be leached from the soils in conjunction with H^+ displaced cations.

Johnson found in his field studies that adsorbed sulphate becomes increasingly fixed and unavailable in the soils with time, through slow chemical reactions with sesquioxides. It is hypothesized that these accumulations are occurring by soil sulphate adsorption. Johnson suggests that long-term field studies are probably the most suitable way to evaluate a soil's resistance to leaching by H_2SO_4 .

A point of interest in the study is that unspecified laboratory studies show sulphate adsorption was reversible but field results indicate that over one half of the adsorbed sulphate was in non-extractable form. This discrepancy between field and laboratory results should serve as a warning to use caution in applying laboratory studies to field situations.

In conclusion, Johnson found that cation leaching from soils due to atmospheric sulphuric acid inputs cannot occur unless sulphate is mobile in the soil or it displaces another anion that is mobile in the soils.

(3) Atmospheric Sulfur: Its Effect on the Chemical Weathering of New England
N.Johnson, R.C.Reynolds, G.E.Likens; *Science*, Vol. 177, 1972, pp.514-516

Contemporary precipitation over New England is pervaded by 3 to 4 mg/l of sulfate, mostly in the form of H_2SO_4 , which is sufficient to lower the pH of the ambient rain and snow to about 4.1-4.4. By comparison, geologically normal precipitation saturated with CO_2 is much less acidic, pH 5.7.

Simple mass action considerations lead one to expect that weathering rates at pH 4.0 should proceed faster than at pH 5.7. However at Hubbard Brook the weathering reactions are relatively incomplete with the pH of runoff water still quite acid (pH 5.15). The specific cause for the relatively slow weathering at Hubbard Brook is not clear. However, a contributing cause may be the maturity of the soil. The weathering reactivity of the mineral grain has probably been reduced by microscopic coatings of aluminum and clay which act as diffusion barriers between weathering solutions and the interior of mineral grains.

In conclusion Johnson et al explain that cationic denudation of the upland areas of New England does not appear to be unduly accelerated at the present time as a result of artificial acidification of its precipitation. These findings support Wiklander's (1973/74) hypothesis that mature, podzolic soils are not greatly affected by acidic precipitation. The authors of this paper stress that new studies are required to fully reveal the mechanism and rates of chemical weathering in aqueous systems dominated by sulfuric acid.

(4) Soil Resampling and pH Measurements After an 18-Year Period in Ontario
S.N. Linzon and P.J. Temple; *Proceedings of an International Conference*, Norway, 1980, (in press)

The authors present several theories regarding the sensitivity of different soil types to acidic precipitation. It is explained that soils take many years to develop and it may be too early to detect changes due to acidic precipitation at this time. There is much disagreement in the literature concerning the effect of acidic precipitation on forest productivity. Details of this are provided in the paper.

To test the hypothesis that soil pH is lowered by acidic precipitation the 1960 Soil Survey of the Parry Sound District, Ontario, was reexamined in 1978. In most cases pH data are the same for both 1960 and 1978. The only soil series to demonstrate a decline in pH over the 18-year period was the Magnetawan Series. The pH of the A_0 horizon dropped from 5.7 in 1960 to 4.8 in 1978. This was the only non-podzolized soil and it had pH above 5.0 in all horizons in 1960, all the other soils are podzolized with pH's below 5.0 in the A_0 horizon..

The authors tentatively conclude that acidified soils are not readily altered by acidic precipitation and that drainage through these soils to surrounding water bodies may be as acidic as incoming precipitation. It is emphasized that although the lakes in the Canadian Shield may be sensitive to acidic precipitation the terrestrial ecosystem may not be as susceptible to change.

This is just preliminary work and a more detailed examination of other soil parameters such as cation exchange capacity, percentage organic matter and the concentration to exchangeable bases and metals is under study.

(5) Acid Precipitation: Chemical Changes in the Soil

N. Malmer; Ambio, Vol. 5, No. 5-6, 1976, pp. 231-234

This article deals with the chemical effects arising in the soil as a result of the acidification of the precipitation, especially in relation to conditions in the Scandinavian countries. The major portion of this paper discussed mobilization of elements in the soil due to acid precipitation and will be found in the appropriate section of this bibliography.

Malmer in his discussion of "susceptibility of different soil types" states that "It is highly improbable that all soils are equally susceptible to acid precipitation. Cation exchange capacity, soil texture and soil structure vary widely" (233). Malmer emphasizes that cultivated soils due to the application of fertilizers, will behave differently than forest soils. However, he feels that fertilizers will have a greater acidifying effect than the acid precipitation, a theory that is opposite to that proposed by: Wiklander, (1973/74); Wiklander (1975); Norton (1977); McFee et al (1977); Frink and Voight (1977); McFee (1979), and Wiklander (1980). The alternative theory suggests that cultivated soils have a high buffering capacity due to the high cation content of fertilizer. Malmer does admit, however, that natural soils with high pH and base saturation have been most resistant to acid precipitation but attributes this merely to the Ca content.

Based on theoretical research and experimental studies, Malmer concludes that the most adverse effects of acid precipitation are to be expected on soil types

transitional between brown earths and podzols. The replacing efficiency of the hydrogen ion causes fewer leaching effects in very acid soils than in only slightly acid or neutral ones. However, Malmer then explains that due to the changes in the chemical potential of K, Mg, and Ca at different values of pH the relative losses from leaching will be greater the lower the base saturation and the cation exchange capacity.

(6) Sensitivity of Soil Regions to Long Term Acid Precipitation

W.W. McFee Presented at the 1979 Life Sciences Symposium
"Potential Environmental and Health Effects of Sulfur
Deposition" October 14-18 1979, Gatlinburg, Tennessee, 22pp.

also: Sensitivity of Soil Regions to Acid Precipitation
EPA-600/3-80-013, January 1980, 179 pp.

McFee feels that since acid precipitation is so widespread and the potential harm to soils is subtle, there is a need to concentrate our research efforts on areas most likely to be susceptible. From a summary of recent reports McFee presents 8 known and expected effects of acid precipitation on soil: 1) natural soil formation processes in humid regions lead to acidification and acid precipitation accelerates this process; 2) the sensitivity of soils to acidification by acid precipitation depends on the soil buffer capacity and pH; 3) very acid soils are less sensitive to acidification; 4) acid inputs increase leaching of exchangeable plant nutrients; 5) acidification slows many soil microbiological processes, such as N fixation, decay of plant residues and nitrification; 6) acid precipitation increases the leaching losses of Al; 7) amendments used in crop production overshadow acid precipitations influence on the soil; 8) there are large uncultivated areas that have soils that are poorly buffered and potentially sensitive to acid precipitation.

In this paper criteria for ranking soil sensitivity to the effects of acid precipitation are discussed. A ranking scheme based on cation exchange capacity and presence or absence of carbonate in the top 25 cm of soil and presence or absence of flooding was devised. From a review of the literature (Wiklander 1973/74; Bache 1980, Reuss 1977) McFee feels that it is apparent that the following 4 parameters are important in estimating soil sensitivity to acid precipitation: 1) the total buffering capacity or cation exchange capacity which can be estimated by the clay and soil organic matter; 2) the base saturation of that exchange capacity which can be estimated by the pH of the soil; 3) the management system imposed on the soil (cultivation, fertilization, flooding); 4) the presence or absence of carbonates in the soil profile.

Five map units varying in potential sensitivity and percentage of the area considered sensitive were used to map the eastern United States. Maps of New York, North Carolina, West Virginia, Pennsylvania and Indiana are presented. It is recognized that other factors could be considered to improve the ranking scheme and that land use, which is ignored in these maps, has an effect overshadowing that of acid precipitation. McFee explains that the maps should be useful in research planning and in selecting areas for intensive study.

McFee states that he is aware that the criteria used are arbitrary and that arguments can be made for different assumptions about inputs, depth, percentage base saturation, etc. He feels, however, that our limited knowledge of the effects of acid precipitation on soils and the generalized information available on the distribution of soil association and their properties make this a reasonable first approach to mapping sensitive soil regions. It should be stressed that this is the first published report where the distribution of susceptible soil regions have been mapped as opposed to hypothesizing the spatial distribution of susceptible soils based on purely theoretical or experimental knowledge.

(7) Air Pollution Impact on Soils

W.W. McFee and J.M. Kelly; Soil Conservation Society of America, Vol. 32, 1977, pp. 203-207

This paper is a reiteration of the findings of McFee et al (1977) as well as a literature review of acidic precipitation and soil articles and papers on metal contamination in soils. In the section entitled "Soil Acidification" McFee and Kelly summarize the work of Reuss (1975), Tamm (1976), Malmer (1976) and Abrahamsen et al (1976). They conclude from the literature that soils, in general, are more resistant to damage from acidic precipitation than lakes and vegetation and that agricultural soils will not be significantly affected. The authors emphasize that a system of monitoring these effects in the field is needed and that additional controlled experiments should be performed to predict future effects more easily.

McFee and Kelly also explore the literature on metal contamination of soils by aerial deposition. This has caused localized damage only near industrial sources. However, there is evidence of long range transportation and deposition on soils which should be considered a threat.

The authors stress that the soil not only receives particulate matter and precipitation from the air, but it releases gases, adsorbs gases and provides much of the dust in the atmosphere.

There are 45 papers cited in the reference section. This is a fairly complete

list of articles published in the early 1970's on both the effect of acidic precipitation on soils and metal contamination of soils.

(8) Ion Adsorption Isotherms in Predicting Leaching Losses from Soils due to Increased Inputs of "Hydrogen" Ions - A Case Study

S.I. Nilsson; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.Hutchinson and M.Havas (eds.), Plenum Press, 1980, pp.537-552.

Nilsson presents a theory of ion adsorption isotherms which have potential use in predicting leaching losses from soils under increased inputs of H^+ ions. This paper is reviewed in greater detail in the section of this bibliography on "Mobilization Of Elements In Soil".

Nilsson discusses data on calcium-based isotherms, derived from chemical potential calculations of Ca relative to Mg and K from a field site in Sweden (Lisselbo). This site has received experimental perturbations of sulfuric acid and/or liming over a 7 year period. This preliminary data indicated that, although within-treatment variation was large, the concept appeared to have potential as an index of sensitivity. Adsorption isotherms might be used to classify forest soils according to their "acidification sensitivity" in a more precise manner than have been made by stating threshold values for acid deposition, according to the author.

(9) Acid Rain - A Plus or Minus to Agriculture

R. A. Pennay ; Unpublished report, September 24, 1980, 8 pp.

The author attempts to determine the effect of acidic precipitation on agriculture in 4 pages of text. The theme is interesting as applied research is scarce in the acidic precipitation literature to date. A large portion of the article is about vegetation and agricultural yield changes due to simulated acid rain. Although most of the soil work is strictly theoretical it will be briefly reported.

Pennay begins the article by stressing that the effect of acidic precipitation on agricultural soils has not been fully determined at this time. He goes on to discuss application of lime to soils, specifically in Pennsylvania. Acid rain is seen as contributing to the cost of agricultural production via the cost of neutralizing soil acidity. However, nowhere in the paper does Pennay demonstrate that acid rain will in fact decrease the pH of the soil.

Pennay concludes that the total effect of acidic precipitation on agriculture is not known and further study is needed. He then describes the world as a very

simple system and states that when man alters any conditions of the system (i.e. acid rain) we can expect changes to occur in plant life. This is a statement Pennay fails to verify in this paper.

(10) Podzolization: Mechanism and Possible Effects of Acid Precipitation

L. Petersen; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas(eds.), Plenum Press, 1980, pp. 223-238

In this report Petersen considers the mechanism and possible effect of acid precipitation on the podzolization of soils. Much of this paper deals with the mobility of elements in the soil and is reviewed in another section of this bibliography.

Petersen explains that acid precipitation may affect the process of podzolization in two ways: 1) since an acid surface soil reaction is a pre-requisite for podzolization additional increments of acid could start the process at an earlier date on susceptible soils; and 2) additional acid inputs could amplify podzolization by increasing the thickness of the eluvial A horizon and further depleting surface soils of nutrients.

The time required for development of a podzol may vary from a few hundred years to several thousand years. Even the shorter period is long as compared with the period in which observations on the occurrence and effects of acid precipitation have been carried out. Petersen does not expect that it is possible as yet to make direct observations on the effect of acid precipitation on podzol development.

(11) Sensitivity of Different Soils to Acid Precipitation

L.Petersen; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.Hutchinson and M.Havas (eds.), Plenum Press, 1980, pp.573-577

In this paper a very general evaluation of the relative sensitivity to acid precipitation of some of the soils of the world is attempted using the American and FAO/UNESCO system. Important properties to consider in such an evaluation include base saturation status of soils, buffer capacity and carbonate content.

Entisols (Regosols in Canada) are slightly developed soils and include soils formed on till, solid rock, and lacustrine sediments. Because of this high degree of variation their sensitivity to acid precipitation cannot be evaluated.

Inceptisols (similar to Brunisols in Canada) vary with respect to properties

important to the sensitivity to acid precipitation. Sandy species will be most sensitive.

Aridisols (no Canadian equivalent) are soils of deserts and other dry regions. The saline arid soils may benefit from acid addition as their natural pH is too high for plant growth. Due to low amounts of precipitation they will receive only small amounts of acid and are, therefore, not likely to be affected by acid precipitation.

Mollisols (Chernozems in Canada) are soils with considerable humus content and subject to little leaching. Their base saturation is high and, therefore, not likely to be sensitive to acid precipitation.

Alfisols and Ultisols (no equivalent Canadian classification, closest to Luvisols) are soils with an argillic (clay rich) horizon. Alfisols have a high base saturation percentage. They are not very sensitive to acid precipitation. On the other hand, the low base saturation of Ultisols may make them more sensitive to acid precipitation.

Spodosols (Podzols in Canada) are acidic with sub-soil (horizon) accumulations of sesquioxides and humus. In another paper Petersen (1980) explained that additional acid inputs to Spodosols could amplify podzolization. On the other hand, Wiklander (1973/74, 1980) predicts no significant change in these acid soils due to acid precipitation.

Oxisols (laterites) all have low cation exchange capacity and considerable clay content (kaolinite) and low humus content. They have therefore, rather low pH values and low buffer capacity. According to Petersen acid precipitation could have a significant effect on these soils. One could argue, however, that since Oxisols are already acidic, acid precipitation will not cause significant changes. At present they are not subject to acid precipitation due to their locations in the tropics.

Vertisols are black heavy clay soils which occur in the tropics and have no Canadian equivalent. They have a high degree of base saturation and are not affected by acid precipitation.

Histosols are soils which consist of organic matter (peat). Base saturation of these soils varies widely. Acid precipitation is expected to have a very small effect, if any, on histosols due to their high buffer capacity.

Arenosols are sandy soils with low buffer capacities. These may be relatively sensitive to acid precipitation.

Although Petersen's discussion is pedologically sound, in the concluding remarks he states that Entisols, Inceptisols, Ultisols, Spodosols and Oxisols are all sensitive to acid precipitation. Spodosols and Oxisols being quite acidic already, are not likely to be very sensitive to acid precipitation according to Wiklander's theory (1973/74, 1980). Entisols, if formed on any material other than sand will

also not likely be very susceptible to changes due to acid precipitation.

Petersen recognized that a major obstacle in preparing a paper like this is that highly different soil classification systems are used in different parts of the world. In many instances, it is extremely difficult or even impossible to identify equivalent soil entities in the different systems. It should be stressed that this is just a general paper and as Petersen states no conclusions should be drawn from the considerations mentioned in this paper as to the absolute effect of acid precipitation on the soils.

(12) Acid Precipitation and Forest Soils

C.O. Tamm; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 367-369

According to Tamm, the effect of acid precipitation on soil depends at first to what extent acid is really adsorbed by the soil and on the changes in the substances with actual or potential acidity leaving the soil. If added H_2SO_4 leaves the soil as gaseous H_2S there is no net acidification, however, if SO_4^{2-} ions are precipitated through the soil, acidification does occur.

The impact on the soil depends on the soil properties, particularly the amount of exchangeable cations in the soil. On the average, a soil with low base saturation is acid and a soil with high base saturation is neutral or alkaline. Tamm agrees with Wiklander's (1973/74) hypothesis that an input of more H^+ ions to an already acid soil means relatively small change and soils with high base saturation have large buffer capacities. It is the slightly acid soils with both low exchange and buffer capacities which may be sensitive to acid precipitation.

Tamm explains that different soil colloids have different affinities for various types of ions. The affinity is pH dependent and thus has to be taken into account in a discussion of soil acidity. Tamm also discusses the importance and influence of different soil horizons and the transport of water through the soil profile. Very often minerals weather more intensely in the upper more acid horizons than further down and some of the weathering products may be moved downward and either leached from the profile or precipitated in lower horizons.

Differences between how agricultural and forest ecosystems affect nutrient cycling in soil systems are outlined. A characteristic trait for forest ecosystems as compared with agricultural ecosystems is the relatively close nutrient circulation during most of the rotation period in a managed forest. Some of the effects of acid precipitation may accumulate for a long period of time and then become evident in connection with a regeneration phase in the forests.

Tamm stresses that we have to look more carefully for possible effects on

(122)

processes restricted to soil particle surfaces if we are to evaluate correctly the impacts of acid precipitation.

(13) Production and Consumption of Hydrogen Ions in the Ecosphere

B. Ulrich; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp.255-282

Before studying the effects of hydrogen-ion production due to acid precipitation the author stresses that hydrogen ion production under undisturbed conditions should be known. In this paper an attempt is made to develop a general scheme for estimating man-made as well as natural sources of H ions in terrestrial ecosystems.

Detailed explanations of the chemistry of H^+ input by precipitation in the pre-industrial time, effect of H^+ input on roots and the effect of ion uptake and mineralization are presented. The author then used data from a beech and spruce forest ecosystem in Solling, West Germany to demonstrate how natural acid production in an ecosystem can be calculated from phytomass build up, decomposition and export. It is important to find out whether nitrogen uptake occurs as NH_4 or NO_3 . Mineralization and uptake processes in the soil organic layers are coupled in such a way that the net change in hydronium ion flux caused by percolating water is close to zero. Ulrich also discusses buffering ranges of mineral soils and some aspects of aluminum chemistry in acid soils. He finds that SO_2 and NO_x emissions lead to substantial changes in the chemical soil state in the uppermost soil layers.

Ulrich presents a new approach to the problem to studying the natural cycle of H^+ ions in the ecosystems. He stresses that the effect of air pollution on an ecosystem can only be assessed by comparing the situation today with the situation some decades ago.

(14) The Acidification of Soil by Acid Precipitation

L. Wiklander; Grundforbattring, Vol. 26, No. 4, 1973/74, pp. 155-164

This is perhaps the first published paper solely on the topic of acidification of soil due to acid precipitation. It is here that Wiklander first presents his much quoted classification of the sensitivity of various soil categories to acid precipitation according to: 1) buffering capacity against pH-change; 2) H^+ retention; 3) replacing efficiency of H^+ for exchangeable base cations; and 4) adverse effects on soils.

Wiklander explains that acid precipitation contains strong acids, mainly H_2SO_4 , HNO_3 , and HCl and also NH_4 . This paper aims to elucidate the principal reactions in the soil that are induced by acid precipitation and to discuss the sensitivity of soils in this connection. Some experimental data supporting the inferences drawn are also presented. Wiklander stresses from the outset that the evaluation of the influence of acid precipitation is difficult and many of the conclusions drawn are dubious and may even be erroneous.

Acidification of soils involves several consecutive reactions: 1) soluble salts are leached to deeper horizons by percolating excess water; 2) soluble compounds (CaCO_3) are gradually brought into solution; 3) soil pH and base saturation decrease markedly. Wiklander believes that the replacement of base cations from the surface of the soil particles is the most important process of the acidification of soils. This reaction is caused by the replacement of exchangeable base cations, such as Ca, Mg, K and Na by H_3O^+ , from the infiltrating precipitation. The replacing efficiency of H_3O^+ is determined by the soil properties, ex. pH, degree of base saturation, cation exchange capacity, and acidic strength of the cation exchanging groups, as well as by the concentration of H_3O^+ , NH_4^+ and Ca, Mg, Na and K in the precipitation.

Acid precipitation and nitrified NH_4 have a strong cation replacing and dissolving effect in neutral and slightly acid soils. In strongly acid soils this effect is weaker. Wiklander explains that the presence of carbonates and ferromagnesium minerals buffer against pH-decrease as do the clay fraction and humus, if the base saturation is high. Calcareous soils and cultivated soils show high buffering and low sensitivity whereas uncultivated slightly acid, sandy soils and loams are more sensitive to acidification.

Wiklander disagrees with the findings of Jonsson and Sundberg (1972) that a decrease in forest productivity in Sweden (1950-1965) was caused by an assumed lowering of cation nutrients in the podzols as a result of sulfur deposition. In 1973 Wiklander resampled an iron-humus podzol in Sweden that had been originally studied in 1934. Soil pH was determined with water, 1 M KCl and 0.01 M CaCl_2 . Wiklander found no significant pH change had taken place in the last few decades, a finding Malmer (1976) claimed was dubious due to the problems inherent in resampling other's work.

Wiklander concludes that increased deposition of sulfur has apparently not sufficed to change the stable acid conditions of Swedish podzols as registered by soil pH.

(15) The Role of Neutral Salts in the Ion Exchange Between Acid Precipitation and Soil

L. Wiklander; *Geoderma*, Vol. 14, 1975, pp. 93-105

In an earlier report (Wiklander, 1973/74) the acidification of soils by atmospheric deposition of strong acids was discussed. Also the effect of deposited neutral salts on this process was briefly treated. There seems to exist some confusion among researchers about the role of neutral salts in the ion exchange processes occurring in connection with acidification of soils by acidic precipitation. In this paper the salt effect is further discussed and demonstrated by some experimental data. For a detailed description of these leachate experiments see the section of this bibliography on "Mobilization of Elements in Soil".

It was found that the positive salt effect on the base status of soils is more pronounced in very acid soils, such as podzols and some brown earths (Brunisols), than in slightly acid soils. In soils with $\text{pH } 6^+$, neutral salts have no practical importance in reducing the acidification effect of atmospheric acidic compounds.

The adverse effect of acid precipitation, therefore, is likely to be less in very acid soils, such as podzols, than a slightly acid and neutral soil with low buffering capacity against pH change. Soil texture and calcite content are very important factors in this respect as fine material and calcite increase the buffering of a soil.

Theory and experimental results support the statement that studies on the acidification of soils by addition of H_2SO_4 , without consideration of the natural atmospheric deposition of neutral salts, will exaggerate the harmful effect on acid soils.

(16) The Sensitivity of Soils to Acid Precipitation

L. Wiklander; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp. 553-568

According to Wiklander, acidification of soils means a decrease of the pH and base saturation caused by internal production and external supply of protons (H^+). He stresses that the effect of acidifying substances in precipitation depended relatively little on the amount of hydrogen ion inputs as compared to the susceptibility of the soils.

Based on the ion exchange theory, ion exchange experiments and leaching of soil samples, Wiklander feels that little or no change would be expected on calcareous, well-buffered soils with a pH above 6 or on acid, moderately buffered

soils below pH 5, whereas poorly buffered soils in the range of about 4-6 are relatively susceptible. Clay soils buffer well and are moderately sensitive. Calcareous soils retain their pH until the carbonate is dissolved. In cultivated soils the mineral acid fallout only means a slight increase in the lime requirements.

Other factors mentioned that affect soil susceptibility to acid precipitation include climate (especially excess of precipitation over evapotranspiration), topography, and soil structure, both of which influence the amount of runoff relative to soil percolation and thus the time of contact between acid percolating solutions and cation exchange sites in the soil.

Wiklander noted that atmospheric deposition was not the only source of H^+ inputs, the others being: 1) acid root exudations; 2) carbonic acid produced from the high CO_2 tensions in the soil; 3) the oxidation of reduced S and N compounds; and 4) the presence of acid humic material and plant litter.

Much of the information discussed by Wiklander (1973/74) is presented again in this paper, with few alterations.

C. EFFECT OF ACIDIFICATION ON SOIL MICROORGANISMS

A vast number of organisms live in the soil. The bacteria are the most numerous and are classified on the basis of their energy source. Heterotrophic bacteria require organic compounds for their energy. Autotrophic bacteria obtain their energy from transformations of organic compounds. Soil actinomycetes resemble moulds and are an aerobic, heterotrophic organism. They are sensitive to acid soils, very few survive below pH 5.0. There are 690 species of fungi in the soil. They are heterotrophic and aerobic organisms. Fungi grow best near neutrality but are more tolerant of acidic conditions than bacteria or actinomycetes. In acid soils the fungi have little competition and are the major group of microorganisms present. Findings concerning the effect of acidic precipitation on soil microorganisms are inconsistent. This is an area where much more research is required.

(1) Impacts of Acid Precipitation on Coniferous Forest Ecosystems

G. Abrahamsen, R. Horntvedt and B. Tveite; SNSF-Project, Research Report No. 2, 1432 Aas-NLH, Norway, 1975, 15pp. also in Water, Air and Soil Pollution, Vol. 8, 1977, pp. 57-73

This paper summarizes the three years of results from Norwegian studies which commenced in 1972. Artificial acid "rain" and lime were applied to field plots and lysimeters. The majority of this report is reviewed in the section on "Mobilization of Elements in Soil" only the information on soil microorganisms will be presented here.

Soil samples collected from the field experiment in October 1974 were extracted for enchytraeids (Oligochaeta). Other groups of soil animals were not considered.

Statistical analyses did not reveal any significant influence of the various treatments on the total abundance of enchytraeids. The three main species, however, seem to respond differently to the various treatments. Cognettia sphagnetorum has been significantly reduced in number by liming but not by the simulated acid rain. Enchytronia parva increased in number by increasing the acidity of the rain at high lime levels and decreased with increasing soil acidity at a low lime level. The abundance of Enchytraeus norvegicus was not influenced significantly by any treatment.

(2) Effects of Artificial Acid Rain and Liming on Soil Organisms and the Decomposition of Organic Matter

G. Abrahamsen, J. Hovland, S. Hagvar; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp. 341-362

This paper is an account of several studies carried out in Norway concerning the effect of artificial acidification on decomposer organisms and decomposition of organic matter.

All experiments were located on flat plains of glaciofluvial sediments deposited above the marine limit. The deposits are 60 m thick in some places and sandy. All experiments include treatments with 25 or 50 mm/mo of artificial rain (groundwater), applied during the frost-free period (approximately 5 times a year). The pH of the "rain" was adjusted with sulphuric acid. In-depth descriptions of the experiments are found in Abrahamsen et al (FR 4/76). Fungi from decomposing litter were isolated and their growth measured at different H^+ concentrations. Soil animals were extracted from soil, samples taken from the laboratory and field experiments with application of simulated acid rain and lime.

In coniferous forests located on podzolic soils the abundance of Enchytraeidae (mainly Cognettia sphagnorum) and Collembola were found to increase after acidification. Among Acarina, the numbers of Mesostigmata tended to be reduced by acidification, while the abundance of Brachychthoniidae (Oribatei) appeared to increase. In field experiments liming reduced the abundance of Enchytraeidae, Collembola and Acarina.

Decomposition experiments were carried out with needles of lodgepole pine and Norway-spruce. Cellulose, aspen wood and raw humus material have also been studied. The results indicate that the initial decomposition of plant remains is influenced to a small degree by pH variation in artificial rain between 5.6 and 2.0. The decomposition of older organic matter such as raw humus material, might be more sensitive to acidification. Liming significantly increased the decomposition rate of raw humus. The authors conclude emphasizing that the effects observed were produced with much higher concentration of hydrogen ions than found normally in precipitation, and therefore are not directly applicable to interpretation of the acidic rain problem. It was suggested that long term studies with more realistic inputs of hydrogen ions are necessary in order to assess the effects of current levels of input on decomposition processes.

(3) Effects of Acidity on Microorganisms and Microbial Processes in Soil

M. Alexander; In: Effect of Acid Precipitation on Terrestrial Ecosystems,

T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp.363-374

This paper is an overview of the effects of acidity on microorganism and microbial processes. Alexander explains that microbiologists have long been interested in effects of acidity, and that there is an enormous literature on the subject. However, the areas of ignorance are still quite large. He begins the review by listing the six major microbial groups in soils (bacteria, fungi, actinomycetes, protozoa, algae and viruses) and their essential functions: 1) microorganisms are essential for plant growth; 2) microorganisms are also critical for creating and maintaining many of the characteristics associated with soil structure; 3) the microflora is also critical in preventing excessive accumulation of organic matter; 4) the maintenance of environmental quality also requires an active microflora.

Alexander noted that studies in microbiological processes are typically done in pure culture in the laboratory and that there are serious problems in trying to directly extrapolate these studies to the field because of difficulties in identifying the active population of microorganisms in the field, possibilities of shifting microbiological populations as soil chemical conditions change, and possibilities of a variety of microsites which differ in pH and other conditions within the soil matrix.

In general, nitrifying bacteria are very sensitive to acidity. Their activity falls rapidly with decreasing pH and is undetectable below pH 4.5. The total bacterial community is reduced in abundance as are individual physiological groups. The actinomycetes, which taxonomically are also considered to be bacteria, are generally less abundant as pH falls. The relative abundance of fungi, assessed by counting procedures, rises, an increase that may be associated with the lack of competition from other heterotrophs at the lower pH level. The pH of the soil also influences specialized population that colonize the root surfaces.

One effect of soil acidification of special concern to Dr. Alexander is that of the products of microbial activity. For example, N_2O emissions for denitrification increase with decreasing pH and N_2O is destructive to the ozone layer.

Alexander stresses that short term studies of any stress factor may be misleading because microorganisms may become acclimatized to changes in pH.

(4) Soil Organisms and Litter Decomposition in a Scots Pine Forest - Effects of Experimental Acidification

E.Baath, B.Berg, U.Lohm, B.Lundgren, H.Lundkvist, T.Rosswall, B.Soderstrom, A.Wiren; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.Hutchinson and M.Havas (eds.), Plenum Press, 1980, pp.375-380

According to the authors, the aim of the present study was to examine the extent to which soil biological properties, such as amounts of different soil organism populations, as well as decomposition rates, were affected in a field experiment with dramatically increased acidification.

The investigation was performed in a Scots pine forest on a moraine in Northern Sweden. The soil is a well developed iron podzol. In some plots the soil acidity was changed by addition of dilute H_2SO_4 (50 kg/ha/yr), (150 kg/ha/yr) for a period of 7 years.

Preliminary results indicate a decrease of "active" fungi mycelium in the acidified plots indicating a reduced decomposing potential. The bacterial biomass showed similar changes with a more pronounced decrease than fungi.

The increase in total mycelium could be an effect of a lower decomposition rate of fungal hyphae. The changed number of soil microarthropods might also have had an influence on this process.

The changed acidity caused a decrease in the enchytraeid population, which was dominated by Cognettia sphagnorum. A species of the genus Trachytes and adults of Oppia obsoleta showed a decrease in the acidified plots. The dominant Collembola species showed a significant increase in the acidified plots compared to the control. Most of the species showed no significant differences between control plots and the acidified ones.

The bacterial population from the plot with 150 kg/ha/yr H_2SO_4 consisted of a larger proportion of spore formers (49%) than did the populations from the control plot (10%), and they had a larger proportion of chitinolytic, proteolytic and amylolytic bacteria.

The authors concluded that "acidification can have marked influence on the soil biota" although they had earlier stated that "most of the species showed no significant difference between control plots and acidified ones". They do admit that the relevance of the results obtained in this investigation in relation to normal field situations could be a matter of discussion.

(5) Influence of pH on Inhibition of Bacteria, Fungi and Coliphages by Bisulfite and Sulfite

H. Babich and G. Stotzky; Environmental Research, Vol. 15, 1978, pp. 405-417

The authors explain that much of the research into the influence of SO_2 on the biota has focused on the effects of acid rain and has ignored the potential effects of HSO_3^- and SO_3^{2-} . Therefore, studies were performed to evaluate the influence of HSO_3^- and SO_3^{2-} on the growth of bacteria, fungi and coliphages.

Varieties of fungi, bacteria and coliphage were grown in petri dishes and maintained at various pH's from 3 to 8. Detailed descriptions of the experiments are provided in the paper.

All bacteria studied were more tolerant of higher concentrations of HSO_3^- and SO_3^{2-} than were the fungi studies. The growth of fungi and bacteria was inhibited to a greater extent by HSO_3^- than by equivalent additions of SO_3^{2-} . Increases in the concentration of SO_3^{2-} resulted in a gradual decline in bacterial growth, whereas increasing the concentration of HSO_3^- resulted in an "abrupt" decline in growth after a critical concentration was exceeded. The authors feel that the toxicity of HSO_3^- toward microorganisms and viruses may be a reflection of the damage exerted on several levels of biochemical and cellular complexity. The toxicity of HSO_3^- and SO_3^{2-} to coliphage, bacteria and fungi was pH dependent. As the pH of the medium was decreasing, the toxicity of both anions increased.

The results of this paper indicate that as well as studying the detrimental effects of acid rain (i.e. the action of H^+) the adverse effects of the anionic solubility products of SO_2 (HSO_3^- , SO_3^{2-}) must be studied.

(6) Impacts of Acid Precipitation on Forest and Freshwater Ecosystems in Norway

F.Braekke (editor) SNSF-Project, Research Report No. 6, 1432 Aas-NLH, Norway, 1976, pp. 26-63. Effects of Acid Precipitation on Coniferous Forest

G.Abrahamsen, K.Bjor, R.Horntvedt, B.Tveite.

This report is intended as a summary of the results of Phase I of the SNSF project covering the period July 1972 - December 1975. A more thorough discussion of the results by Abrahamsen et al on the effects of acid precipitation on coniferous forest soils will be found in the section on "Mobilization of Elements In Soils". Only the information pertaining to soil microorganisms will be presented here.

The authors state that the soil fauna in the podzols of Nordic conifer forests are dominantly mite (Acarina), springtail (Collembola) and enchytraeids (Oligochaeta). Consistent results from the acid and lime treatments on enchytraeid population were not obtained. The results from the podzol experiment indicated a population increase when the amount of H^+ ions applied increased from 0.5 me to 55 me. Further application decreased the population density. In the podzol-brown earth experiment no affect was observed.

(7) Effect of Soil Acidification on the Soil Microflora

R.D.Bryant, E.A.Gordy, E.J.Laishley; Water, Air and Soil Pollution, Vol. II, 1979, pp.437-445

The effects of short and long term acidification on a few Alberta soils were studied with respect to bacterial numbers and total soil respiration.

Soils were sampled 1 m and 200 m from elemental S in a stockpile and in a garden plot. One portion of each soil type was set aside for a laboratory treatment (pH 3.0). This treatment provided information on the short term effects of acidification. The total bacterial numbers from the different soils were obtained by standard plate count on peptone-yeast extract agar. Soil respiration (CO_2 evolution) was measured in a static system by absorbing the evolved gas in standard NaOH solution and determined by precipitation of the formed Na_2CO_3 and 2N $BaCl_2$, followed by titration of the unreacted NaOH with standard HCl. Data were statistically analyzed.

Significant reductions in bacterial numbers were observed in both short and long term acidified soils. Total soil acidity was severely affected in an acid soil (pH 3.0, long term) adjacent to an S block. A soil (pH 6.8) 200 m away from the S block when artificially acidified to pH 2.9 significantly reduced soil activity but not as drastically as found in the long term pH 3.0 soil. A garden soil (pH 7.7) which was also acidified to pH 3.2 showed no significant reduction in total soil respiration rate as compared to its unacidified control soil. This is probably due to its physical structure and biological composition.

These acidified soils when amended with organic substrates demonstrate that certain physiological groups of organisms were severely inhibited by this acid condition. The garden soil study showed no significant difference in soil respiration rates between the unamended acidified and nonacidified soil. This would indicate that the short-term acidification treatment had no affect on biological activity. The organisms responsible for utilization of cellulose, urea and casein were adversely affected, however, as compared to the amended nonacidified garden soil.

This demonstrates the importance of examining more than one parameter when assessing the effect of a potential pollutant on soil activity.

(8) Colonisation by Enchytraeidae, Collembola and Acari In Sterile Soil Samples with Adjusted pH Levels

S. Hagvar and G. Abrahamsen; Oikos, Vol. 34, No. 3, 1980, pp. 245-258

This paper is concerned with the effect of soil acidity on the distribution and abundance of soil animals. Variations in soil pH were produced by lime (CaOH_2) and H_2SO_4 applications. Natural soil or slightly ground raw humus were used as mediums. 150 bags were prepared from each of three soil types and adjusted to three different pH levels. The soil animals were allowed to choose between soil samples of different pH values and to reproduce for a certain period. From each group of 50 bags, 22 were used for extraction of Acari, Collembola and Protura, 20 were extracted for Enchytraeidae, 6 were used for chemical analyses and two for pilot examination before the experiments. Twice a week for 5 months the bags received 10 mm of water with a salt content similar to that found in the rain of southern Norway at pH's 3.5, 4.3 and 5.3.

Detailed results are provided in the report. In summary, though, soil pH significantly influenced the success of colonisation in the following number of species: Collembola 7, Oribatei 8, Mesostigmata 3, Astigmata 1, Enchytraeidae 3, Lumbricidae 1. In all three soils there were reactions in favour of both acidification and of liming. When a species reacted to both lowered and raised soil pH, these reactions were always opposite.

The authors conclude that at present, the most fruitful hypothesis appears to be that there is a correlation between soil pH and reproduction success in several species. Whether this effect is due to H^+ concentration alone, or rather to other factors following it, is not clear.

(9) Effects of Simulated Acid Precipitation and Liming on Nitrification in Forest Soil

J.Hovland, Y.Z.Ishac; SNSF-Project, Internal Report No. 14, 1432 Aas-NLH, Norway, 1975, 15 pp.

The intention of this study is to determine whether nitrification in soil from an experimental area has been influenced by simulated acid rain and by lime application.

Soil samples were collected in October 1974, 40 km north of Oslo, Norway. The soil is a semi-podzolic type and Pinus contorta Douglas trees are stocked in the area. Plots have been irrigated since 1972 with acid "rain", pH 5.6, 4.0, 3.0 and lime at levels of 1500, 3000 and 6000 kg CaO/ha have been added to some of the plots.

Soils were tested for nitrifying bacteria in a medium buffer. Glass perfusion apparatus with a column for soil and a reservoir for the perfusing liquid were used in the nitrification experiment. pH was measured and the samples were analyzed for NH_4 , NO_2 and NO_3 .

Nitrifying microorganisms were found in all soils, whether limed or not. With the perfusion technique used, nitrification took place only in humus samples from plots treated with limestone. The presence of the bacteria can be explained if one assumes that the nitrifying bacteria in acid soils are in microhabitats associated with higher pH.

In limed treatments the amount of nitrate produced was dependent on the buffering capacity of the soil. The nitrification began later in the soil treated with 3000 kg CaO/ha and rain at pH 5.6. Other experiments indicated that soil from the limed field plots have a great potential for nitrification caused by high base saturation and pH.

(10) Effects of Simulated Acid Precipitation and Liming on Pine Litter Decomposition

Y.Z.Ishac and J.Hovland; SNSF-Project, Internal Report No. 24, 1432 Aas-NLH, Norway, 1976, 20 pp.

The decomposition of lodgepole pine needles (pinus contorta Douglas) has been studied in a laboratory experiment. The needles were picked from trees that have been irrigated with simulated acid rain at pH 5.6 or 3.0. The soil beneath some of the trees was limed.

The decomposition of the needles increased with temperature and incubation period. Liming of the soil retarded the decomposition of the needles that have been given rain at pH 3, while irrigation with 50 mm of water per month at pH 3 increased the decomposition compared with 25 mm/month.

When needles were incubated in dilute sulphuric acid, the decomposition was reduced at pH 1.8 compared to the decomposition at pH 3.5. At pH 1.0 no decomposition occurred.

Fungi were isolated from the needles. The different treatments did not seem to affect the composition of the fungal flora of the needles. The fungi were tested for their ability to decompose cellulose. The four most active cellulose

decomposers were Trichoderma harzianum, Coniothyrium sp., Cladosporium macrorcarpum, and a sterile white mycelium. T. harzianum seemed to be more tolerant to acid conditions than the other fungi.

(11) Studies of Acid Rain on Soils and Catchments

J.E. Rippon; In: Effects of Acid Precipitation on Terrestrial Ecosystems,
T.Hutchinson and M.Havas (eds.), Plenum Press, 1980, pp.499-524

Rippon describes the experimental design and some preliminary results of acid rain studies on soil and catchments in England. The results of the catchment studies will be presented in the section on "Effects of Acid Precipitation via Soil on Aquatic Systems", while the results of the lysimeter leaching experiments are located in the "Mobilization of Elements in Soil" section. Only the microbiological information obtained from the pot-scale experiments will be found here.

50 pots were filled with soil from each horizon used in the lysimeter study. Half of the pots received distilled water and the remainder sulphuric acid (pH 3.0). The pot soils were subjected to a range of microbiological tests at six month intervals.

The microbiological numbers are estimated by the Most Probable Number method on plates and tubes. The results were then examined by the principal component technique to identify any affect or trend caused by acid watering.

Preliminary results from pot studies showed no significant changes in bacterial populations, but some tendencies toward pH reduction following acid treatment. No significant effects on CO_2 evolution, enzyme activity or mineralization were noted following acid treatments.

(12) Acid Precipitation: Biological Effects in Soil and on Forest Vegetation

C.O.Tamm; Ambio, Vol.5, No. 5-6, 1976, pp.235-238

Tamm discusses the possible effect on vegetation and soil organisms of moderate but persisting change in the "chemical climate" such as the increase in precipitation acidity observed in Scandinavia in recent years. Just the section on soil microorganisms will be presented here. The forest growth research and nutrient information presented in this paper by Tamm will be found in the appropriate sections of this bibliography.

Tamm reported that acidification inhibited the nitrification process in a forest soil and that the effects on soil respiration and nitrogen mineralization are connected with specific effects of acidification on soil organisms. At the time of this report (1976) results for only one group of soil organisms, the enchytraeids were available (Abrahamsen *et al*, 1975). The Cognettia sphagnetorum had not yet

provided conclusive results but a considerable decrease in the species had been noted with a higher supply of sulphuric acid.

(13) Effects of Application of Sulphuric Acid to Poor Pine Forests

C.O. Tamm, G. Wiklander, B. Popovic; Water, Air and Soil Pollution, Vol. 8, 1977, pp. 75-78

In 1969, the Swedish College of Forestry began field experiments in a pine forest on a glaciofluvial esker 160 km north of Stockholm. These pioneering experiments consisted of leaching field soils with acids and salts. A discussion of the study of pine trees by Tamm will be found in the appropriate section of this bibliography. Some results of the soil incubation experiments by Popovic will be presented here.

A_0 soil horizons were collected from a number of sites in Sweden then incubated in the laboratory. The release of N was measured in all the soil samples every 6 to 9 weeks as was the CO_2 evolution in some soil samples. In addition to the incubation experiments, model experiments in the laboratory were carried out with humus samples from untreated areas in the field.

The results from the model experiments were more consistent than the incubation experiments. Incubation studies demonstrated a depression of the release of CO_2 when either H_2SO_4 or powdered S was added.

Popovic concluded from the CO_2 data available that an acidification of soil decreases microorganism activity. This decrease is apparently more pronounced as regards the immobilization processes (including microbial growth) than in the case of decomposition processes.

Tamm concludes his report on soil microorganisms by emphasizing that knowledge of the importance of soil fauna is very scanty and there is a need for studies of soil organisms other than enchytraeids. Tamm states that even if we find effects of acidification it will still be difficult to interpret them in terms of ecosystem functions.

D. EFFECTS OF ACID PRECIPITATION VIA SOIL ON AQUATIC SYSTEMS

The hydrological cycle is the endless interchange of water between the sea, air and land. Movement of fresh water in the cycle takes place as precipitation, part of which may be received by the stream channel; as water flowing over the ground surface to the streams and rivers; as water flowing through the soil and rocks; and water can also be stored temporarily in the soil. The morphological and chemical components of the soil can affect the water around it. It appears that a number of soil-bound elements such as Al, Mn and often Fe and Hg are readily removed from soils by acidic precipitation. On the other hand, through the dissolution of Al hydroxide compounds and by the leaching of bases, neutralization of acidic precipitation may occur in the soil. Generally, by the time the acidic precipitation first appears as stream flow its acidity has already been greatly diminished. The vulnerability of aquatic ecosystems to atmospheric pollutants depends on pedologic and geologic factors as well as topographic, morphometric, climatic, biotic and anthropogenic ones.

(1) Aluminum Leaching in Response to Acid Precipitation: Effects on High-Elevation Watersheds in the Northeastern United States

C. Cronan, C.L. Schofield; *Science*, April, 1979, Vol. 204, pp. 304-306

The authors present summary data illustrating the unexpected importance of dissolved aluminum in the solution chemistry of ground and surface waters from high-elevation watersheds exposed to regional acid precipitation. It is suggested that aluminum represents an important biogeochemical linkage between terrestrial and aquatic environments exposed to acid precipitation. A more in-depth review of the aluminum mobilization in soils will be found in the section on "Mobilization of Elements in Soils".

Limnological studies in the Adirondack lakes region have indicated that much of the soil-derived aluminum may be transported from the surrounding watershed to acidified lakes. A synoptic survey of high-elevation lakes of the Adirondacks showed that aluminum concentration in acidified lakes are 10 to 50 times higher than concentrations in circumneutral waters in the same region. Toxic conditions for fish may be produced by dissolved inorganic aluminum (0.2 mg/l) even when the pH levels are not physiologically harmful. The increased transport of aluminum to aquatic systems may indirectly affect phosphorus availability through increased inorganic precipitation of aluminum phosphate.

(2) Some Effects of the Acidification of Swedish Lakes

W.Dickson; Verh. Internat. Verein. Limnol., Vol. 20, 1978, pp.851-856

As an introduction to his research the author discusses the acidification of inland waters in Sweden. It has been found that slowly weathering granites and gneisses contribute to low buffering capacities of lakes.

The author explains that when a soil is exposed to acid deposition it acts as a buffer. The runoff water, usually has a higher pH than the water added. Ca and Mg are the most important cations for buffering, however, aluminum can be of great importance with decreasing pH.

Findings of a study done by Wiklander in 1977 are presented. To a lysimeter 100 kg of H_2SO_4 per hectare were added for 5 years. The concentration of aluminum in runoff water increased to more than 1 mg/l but was only 0.2 mg/l in the non-treated soil water.

Increased leaching of Al has also been noticed in the lake water under natural conditions. Above pH 5.5 the solubility of Al is low and excess Al is precipitated. It has been established that organic matter may form complexes with aluminum and may also precipitate humic substances. In some acidic lakes transparency has increased by more than 10 m compared to before acidification. It is hypothesized that the increasing transparency depends on the precipitation of humus due to increased aluminum levels in connection with low pH. Al also easily precipitates dissolved P and Dickson presents findings of a laboratory test to substantiate the theory.

When the soil or water is acidified, aluminum silicate will buffer as it dissolves. However, when dissolved in acid water aluminum will act as a weak acid. Acid lake water with pH 4.1 and 0.45 mg/l Al and 2 synthetic lake waters of pH 4.1, one with 0.5 mg/l Al added, are titrated with a base to a different pH. The same waters are titrated with acid, back to the original pH 4.1. The acid lake and the Al solution needed less acid than the "blank" titration to reach the original pH 4.1. The author concluded that acidic lakes may be regarded partly as solutions of weak acids of aluminum salts and they may be more acidic than is indicated by the pH value.

Unfortunately the paper contains a number of grammatical and spelling errors which detract from the otherwise interesting organization of laboratory studies and field data on aluminum in lakes and soil.

(3) Effects of Acid Deposition Upon Outputs from Terrestrial to Aquatic Ecosystems

E.Gorham and W.McFee; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T.Hutchinson and M.Havas (eds), Plenum Press, 1980, pp.465-480.

The authors comment that the influence of acid precipitation upon terrestrial outputs may be direct, where atmospheric elements pass over or through the soil to waterbodies; or indirect when elements added in precipitation accelerate or retard the process of soil weathering, leaching and organic deposition. The vulnerability of aquatic ecosystems to atmospheric pollutants will depend on climatic, geologic, topographic, morphometric, biotic and anthropogenic factors.

The increasing acidification of streams and lakes in Europe and North America is discussed. It is emphasized that the ratio of lake area to drainage basin and also the adsorption of S and N oxides and degree of neutralization in canopy and soil will determine the balance between acid deposition indirectly on the lake surface and acid deposition transferred from the land. The authors stress that there is an urgent need for mass-balance studies to determine the degree that acids, heavy metals, nutrients, etc. that react with the aquatic ecosystem have originated from direct precipitation or through the soil, vegetation canopy, etc.

Under the heading "Materials Leached From Terrestrial Soil By Acid Precipitation" the findings of Wiklander (1973/74), Abrahamsen *et al* (1976) and McFee *et al* (1977) are presented. In addition, it is explained that liming counteracts acid precipitation effects and weathering by acid precipitation of aluminosilicates in the soil increase Al in the lakes.

The material retained in the terrestrial ecosystem include acids deposited from the atmosphere which are neutralized or exchanged for metal cations in vegetation and soil. Heavy metals are also trapped by vegetation, clay or organic molecules. The supply of nutrient elements from terrestrial to aquatic ecosystems may be lessened as well as enhanced by acid deposition. Acidification is likely to increase adsorption of $\text{PO}_4\text{-P}$ by hydroxy-Al and Fe in the soil. In addition acid deposition is likely to influence the N cycle in forest soils in diverse and opposing ways.

In conclusion, the authors explain that investigation of the effects of acid precipitation upon aquatic ecosystems should be studied by observation and experiments on the whole watershed. Integration of aquatic with terrestrial research programs should be a matter of the highest priority for the future.

(4) Strong and Weak Acids in Surface Waters of Southern Norway and Southwestern Scotland

A. Henriksen and H.M. Seip; SNSF -Project, Research Report No. 17, 1432 Aas-NLH, Norway, 1980, 26pp.

The authors measured the pH, strong and weak acids as well as the concentrations of major ions in lake water samples collected regionally in southern Norway and in small lakes and creeks in New Galloway, Scotland. The techniques and sampling design are outlined in the report.

Henriksen and Seip emphasize that several groups of components may contribute to the weak acid concentration of surface waters. The most important inorganic species are Al and Si components. The organic species contributing to weak acid concentration in lake water originate from the soil in the watershed. An equation based on the assumption that measured weak acid concentrations are mainly due to Al, organic carbon and Si was produced. Upon testing the equation using a multiple regression analysis of the data it was found that Si does not account for much of the variance when concentrations of Al and organic carbon are low. The variance in the weak acid concentration is largely explained by the Al and organic carbon contents.

The authors conclude that because of increased leaching of Al from the soil in areas where deposition of acid components from the atmosphere has risen an increase in weak acid concentration has probably also occurred.

(5) Seasonal Patterns in Acidity of Precipitation and Their Impurities for Forest Stream Ecosystems

J.Hornbeck, G.Likens, J.Eaton; Water, Air and Soil Pollution, Vol. 7, 1977, pp.355-365

Data from nine stations including Hubbard Brook in the northeastern United States were analyzed for seasonal patterns in acidity of precipitation. Precipitation appeared to be most acid in the growing season (May-Sept.) and least acid in winter (Dec.-Feb.). This seasonal pattern of acidity has some implication for the forest-stream ecosystem. Because the maximum acidity occurs when plants are actively growing, the potential for biologic impacts may be at a maximum and will be discussed in another section of this bibliography. In addition, higher summer acidities may have quite an impact on the leaching of nutrients from foliage and soils.

It was found that as precipitation infiltrates the soils at Hubbard Brook and moves towards stream channels it encounters a variety of conditions of soil acidity and chemistry. The organic and A horizons are extremely acid (pH 3 to 4). The upper B horizons have pH's between 4 and 5 and the lower B and C horizons generally have pH's greater than 5. The authors state that cation exchange capacity and degree of base saturation vary greatly between horizons, but provide no quantitative data. As well as the variety of acidities encountered, soil water may also be subject to varying residence times, depending on the season. In summer because evapotranspiration is maximal, soil water deficits occur and the movement of water in the soil is slowed. However, it was found that despite the seasonal variability in H^+ concentration of precipitation, the range of acidity in soil and variation in residence time the streamflow acidity at Hubbard Brook is quite uniform (figures for this are supplied in the paper). This indicates a uniform buffering action by soils and vegetation that reduced the H^+ content of precipitation by a factor between 5 and 10. However, the streamflow has some acidity (H^+ concentration = 10^{-17} uegl $^{-1}$) which suggests, according to the authors, that the weathering reaction in soils is not complete.

(6) Depression of pH in Lakes and Streams in Central Ontario during Snowmelt
 D.S. Jeffries, C.M. Cox, P.J. Dillon; Journal of Fisheries Research Board of Canada, Vol. 36, No. 6, 1979, pp. 640-646

The snowpack that accumulated in central Ontario in the winter of 1977-78 had a pH of 4.0-4.5. The run-off in the spring in three intensively studied watersheds was characterized by a 2-13 fold increase in H^+ content. This depression of pH is most common in areas underlain by Precambrian bedrock that have overburden incapable of buffering the run-off waters.

It was found that cations in the podzolic overburden which were replaced by H^+ include Ca, Mg, Al and to a lesser extent Mn. Elevated Al and Mn levels in many lakes were reported by Scheider *et al* (1979). The possibility that Ca and Mg concentrations are also elevated is harder to evaluate. Levels in the waters in the areas are low but variable (2-10 ppm Ca) and probably dependent on the exact nature and thickness of the thin overburden in individual watersheds.

The authors concluded that a large portion of south-central Ontario may potentially be affected by short-term snowmelt which may induce reduction of pH in streams and littoral zones of lakes. This is a result of two factors: 1) the snow cover by mid-March has a pH of 4.0-4.3; and 2) many of the watersheds are underlain by Precambrian bedrock with only thin and scattered deposits of surficial

till of limited H^+ assimilation capacity. The springmelt may proceed quickly and run-off over partially frozen soils with only partial neutralization taking place, so that the pH's of streams are reduced even in moderately well buffered watersheds.

(7) Acid Rain: Neutralization Within the Hubbard Brook Ecosystem and Regional Implications

N.M. Johnson; Science, Vol. 204, No. 4, May, 1979, pp. 497-499

The author explains that the purpose of this report is to describe and explain the process by which acid rain is transformed into chemically normal streamwater. To this end the chemical characteristics of a small stream, Falls Brook, were monitored over a 3 year period.

In Falls Brook strong acids become successively less important relative to carbonic acid in the downstream direction. The results suggest that Al solubility plays a role in the ionic composition of upstream waters, whereas chemical weathering reactions dominate the composition of downstream waters.

The chemical data from Falls Brook show that the neutralization of acid rain is rapidly and largely (75%) accomplished in the upper soil or regolith by the dissolution of pre-existing Al hydroxide compounds and by the leaching of bases from various biological materials. Thus, by the time the acid rain first appears as stream flow its acidity has already been greatly diminished. Subsequently further neutralization of the strong acids is affected by chemical weathering reactions with the concurrent loss of dissolved Al and the gain of strong bases and silica by the co-existing water. As long as strong acids persist in solution, the neutralization reactions proceed essentially as a base exchange reaction at constant ionic strength. However, when the strong acids are eventually neutralized, carbonic acid will ionize and the ionic strength of the system may increase through open-system carbonation reactions.

In conclusion, Johnson states that due to this mode of acid rain neutralization: 1) probably no sustained acidifying effect will be manifested on major streams, regardless of bedrock type; 2) lakes which receive water from low order streams will tend to be acidified and rich in Al; 3) due to the participation of soil Al in acid neutralization, normal soil formation is disturbed; 4) geologically, no excessive chemical weathering acidity can be attributed to acid rain over the northeastern United States.

(8) Geochemical and Lithological Factors in Acid Precipitation

J.R.Kramer; In: First International Symposium on Acid Precipitation and the Forest Ecosystem, U.S.D.A. Forest Service General Technical Report NE-23 1976 pp.611-617

According to the author the purpose of this paper is to define interactions of soils and rocks with acid precipitation and associated metals in order to predict the resulting water quality.

A calcareous region at pH 8.0 buffers even the most intense loading; an aluminum silicate region with unconsolidated sediments buffers acid loadings at pH 6.5; alumino silicate outcrops are generally acidified. Either FeOOH or alumino silicates are probable H⁺ ion sinks in non-calcareous sediments. It is possible that soluble organic acid can assimilate H⁺ ions at a low pH.

Kind re:acid rain	Alkalinity	pH	Capacity
calcareous rock and soil	2 meq/l	8	very large
fine-grained non-calcareous soil and sediment	0.2-1 meq/l	6-7	can be altered
non-calcareous rock outcrop	0.1 meq/l	4-7	is altered by acid rain

Using Sudbury as a case study to validate his theories Kramer found lakes near Sudbury vary from a pH of 4-8 with total soluble Ni, Cu, Fe and Zn varying from 0.1 to 200 ug/l. The unconsolidated sediment proved to be the key factor regarding the acidity of lakes in the region. The lithological control completely overshadowed the acid precipitation loadings. The acid lakes were found in quartzite rocks which had little or no unconsolidated, calcareous sediment.

(9) Acid Precipitation: Chemical Changes in the Soil

N. Malmer; Ambio, Vol. 5, No. 5-6, 1976, pp. 231-234

This article deals with the chemical effects arising in the soil as a result of the acidification of precipitation, especially in relation to conditions in Scandinavia. Malmer presents a comprehensive review of the Scandinavian literature on acid precipitation and soils at this time (1976). The major discussion of this paper will be found in the section on "Mobilization of Elements in Soils".

Malmer states that increased leaching as a result of acid precipitation is

indicated in studies on inland waters. Scandinavian research has shown that: 1) the amounts of dissolved minerals discharged by Swedish rivers has increased over a 50 year period; 2) in small granitic watersheds the net output of Ca, Mg and Al is directly related to the net input of hydrogen; 3) there is an increase in the concentration of Al in acidified lakes. According to Malmer the changes in the lakes cannot be explained without assuming a considerable increase in the degree of leaching from forest soils. At another point in the same paper Malmer explains that any general connection between the acidification of lakes and soils is not to be expected. Acid precipitation water will readily drain along root channels, the surfaces of stones, etc. without having any close contact with most of the soil particles.

(10) Geological Factors Controlling the Sensitivity of Aquatic Ecosystems of Acidic Precipitation

S.A. Norton; Unpublished manuscript, 1980, 11 pp. text

The author explains that because of the widespread aspect of acidic precipitation it is important to understand the characteristics of the landscape which render an area susceptible to impact. Three major factors are meteorology, pedology and geology. This paper focuses on the geologic controls of impact from acidic atmospheric deposition.

Minerals, when dissolved, are capable of neutralizing excess acid in precipitation according to the number of positive charges in excess of negative charges released into solution. The kinetics of solution are important too in the effectiveness of a particular mineral's capability of neutralizing acid. According to Norton additional geologic and related controls on acidification of aquatic ecosystems include: hydrologic characteristics of the terrain (overland flow, groundwater flow, soil porosity/permeability, residence time of water in soil), distribution of precipitation through time, type of precipitation, thickness of soil, types of soil and age of soil.

The author classified rocks from (1) yield no or little buffering capacity to; (4) infinite buffering capacity. Maps, based on bedrock geology, were then produced which predict vulnerability of aquatic ecosystems to input from acidic precipitation. Field checks of areas underlain by rock types 1 and 2 verified acidification of surface waters in these areas and input on biological systems due to acidic precipitation.

Norton concludes that bedrock geology exerts the most important influence on the extent of acidification of aquatic ecosystems in response to atmospheric

loadings of acid. Soil and vegetative types are of secondary importance. It is stressed that locally, soils may overwhelm bedrock influences.

(11) Sulphur Pollution Patterns Observed: Leaching of Calcium in Forest Soil Determined

L.N. Overrein; Ambio, August 1972, Vol. 1, No. 4, pp. 145-147

This report deals with two aspects of sulphur pollution. First, the deposition pattern around a Norwegian industrial center was charted, and then experiments were conducted to determine the effect of precipitation of varying acidity on the calcium level of forest soils. Most of the results from this paper are presented in the section of the bibliography entitled "Mobilization of Elements in Soil".

Overrein states that the main concern of acid precipitation pollution is that the excess acid deposited on the ground might greatly increase the leaching in soil of plant nutrients out of the root zone and into the groundwater.

A 40 cm deep podzolized forest soil was exposed to 500 mm/mo. simulated acid rain (pH 2.0-6.0) in a series of lysimeter investigations. During the first 20 days of exposure to this "rain" no significant differences were observed with respect to the pH of the leachings. During the remaining part of the 80-day experimental period the acidity of the groundwater gradually increased as the concentration of acid in the simulated acid rain increased. The acidification of the groundwater coincided with the acidification which took place in the soil profile under examination.

(12) Studies of Acid Rains on Soils and Catchments

J.E. Rippon; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas(eds), Plenum Press, 1980, pp.499-524

Rippon describes the experimental design and presents some preliminary results of acid rain research on soil and catchments in England. The microbiological information obtained in the pot-scale experiments will be found in the soil and microorganisms section while the results of the mobility of elements in a lysimeter experiment exposed to acid "rain" will be presented in the appropriate section of this bibliography.

According to Rippon the quality of surface waters depends not only on the composition of the precipitation falling in the drainage basin but also on the reactions that occur as the rain passes through the soil.

Stream water samples were collected every other week for chemical analysis from September 1976 to December 1977 from Snake Pass. The results showed that the first order stream had a pH below 4.5 and often below pH 4.0. The stream 150 m lower was more variable, being neutral during low flow but acid (pH 4.0) at times of high flow.

The high outputs of H^+ and SO_4^{2-} from both streams in the winter 1977 may be a result of the washing through of dry deposits accumulated in the dry summer, and from oxidation processes in the peat as it dried out. It is generally assumed that the sulphate ion is not retained in the systems.

Flow meters and weirs were installed in the Tillingbourne catchment. Soil water samples were also collected. Tillingbourne at its source is more acid (pH 3.7-4.0) than rain (pH 4.1-4.6). The upper stream is seasonal and some acidity is picked up from the acid A and B soil horizons (pH 3.6). Data on sulphur deposition showed that dry deposition accounts for 70% of the sulphur inputs, even in an area as unpolluted as Tillingbourne.

(13) Alternative Sources for Acidification of River Water in Norway

I.Rosenqvist; Science of the Total Environment, Vol. 10, 1978, pp.39-49

The Norwegian SNSF group hypothesized that the increased acidity of Norwegian waters is due to the increased amount of acid air pollutants resulting from the increased burning of fossil fuels. The author argues that the input of hydrogen ions from the precipitation is considerably smaller than the production of hydrogen ions in terrestrial ecosystems. Rosenqvist claims that changes in vegetation and humus, due to changes in agriculture and forestry, are the main reasons for the acidity of freshwater. This paper is also reviewed in the section on "Mobilization of Elements in Soils".

According to the author, normally the amount of precipitation falling directly on the surface of lakes and rivers represents a small part of the annual run-off. Most of the water in the catchment area falls on the soil and passes above or through the geological material. During this period chemical reactions take place between the water phase, the mineral components and the organic matter. Organic humic-rich topsoil will buffer the water phase on the acid side because it represents an ion-exchange system mainly in the hydronium state. These soils react with all ionic components in the rain and melt-water. This results in run-off water of enhanced acidity, independent of the original pH of the rain, according to Rosenqvist. It has been shown that the humus below heather gave pH values around 4, independent of whether the percolating water started off at pH 4.0 or 10. On

the other hand, humus topsoil from a grassfield in the same area gave pH 5.0 to 6.0 under similar conditions.

In conclusion, Rosenqvist showed, through laboratory tests, that for soil-water, even contact times of 30 seconds are sufficient to render the pH of alkaline, neutral as well as acid water into pH values of 4.0 to 4.5, and the amount of exchangeable protons in a normal top soil of organic origin may be equivalent to over 100 years of acids in the present precipitation. Thus, according to Rosenqvist, the humus soil and peat represent strong buffer systems on the acid side, while the increased acidity of precipitation is only causing a minor part of the acidity in rivers and lakes.

(14) Effects of Acidic Precipitation on Precambrian Freshwaters in Southern Ontario

W.A. Scheider, D.S. Jeffries, P.J. Dillon; Journal of Great Lakes Research, Vol. 5, No. 5, 1979, pp. 45-51

Precipitation falling on southern Ontario is as acidic or more acidic (pH 4.0-4.2) than that falling on areas of the world identified as having severe problems related to acidification of freshwaters.

The majority of the lakes in the Haliburton-Muskoka area have very low buffering capacities, and the surficial deposits in many watersheds have limited, in some cases negligible, capacity of neutralizing the acidic precipitation. The authors claim that although it is the geochemistry and geomorphology on a microscale that determines a watershed's ability to buffer acidic precipitation, areas underlain by Precambrian bedrock with little or no surfical deposits must be regarded as being susceptible to the continued input of acidic precipitation.

Manganese and aluminum are good indicators of watershed acidification since they are readily removed from soils by acid precipitation and are naturally low in Precambrian lakes. The authors found that lakes in Haliburton have total Al levels of 49 ug/l. Sudbury lakes that are of intermediate pH (5.5⁺) have approximately the same Al concentration. Background Al levels are unknown but are probably near 2-10 ug/l. Manganese levels (51 ug/l) of Haliburton lakes are higher than background (3 ug/l). Acidified lakes in Killarney have Mn concentrations greater than 200 ug/l while seriously contaminated Sudbury lakes are similar.

(15) Acid Precipitation and Other Possible Sources for Acidification of Rivers and Lakes

H.M. Seip and A.Tollan; The Science of the Total Environment, Vol. 10, 1978, pp.253-270

In response to Rosenqvist's (1978) paper, where he states that the greater part of the increased acidity in surface water is due to ion-exchange processes in an increased mass of raw humus, the authors present an alternative point of view. This report by Seip and Tollan deals mainly with the evidence for a relationship between acid precipitation and acidification of surface water and is also reviewed in the section on "Mobilization of Elements in Soils".

The trends in the recent acidification of rivers and lakes in South Norway are reviewed. Results from regional surveys, studies in small catchments and from percolation experiments are presented.

Their percolation experiments show that the total ion content of the precipitation is important for the pH of the soil leachate. An increase in the H^+ content of the precipitation leads, after some time, to lower pH in the leachate. The authors also found that knowledge about the degree of time of contact between water and soil may be sufficient to obtain equilibrium conditions. Through comparative studies, it was found that most acid lakes in Europe are in the region with the highest deposition of H^+ . A striking similarity is also found by a regional comparison of the sulphate concentration in the precipitation and in the lakes. Seip and Tollan explain that the effect of acid precipitation on lake water depends on the ability of the drainage basin to neutralize incoming acid through such processes as chemical weathering and ion exchanges.

Referring to some results from a watershed study in southern Norway, Rosenqvist (1978) found no direct effect of acid precipitation on lakes. Rosenqvist defines "direct" effect as the case when the acidity in the surface waters is closely related to the pH of the rain with only a small timelag and "indirect" effects occur when the precipitation causes slow changes in the drainage basin. Seip and Tollan feel that it is not surprising that Rosenqvist found no direct effect, as short-term variation of water quality in streams are complex. The effects of evaporation and dry deposition, ion exchange and weathering must all be considered. They hypothesize that ions brought in with precipitation will accumulate in the dry topsoil in the summer and will not be leached out until the soil becomes saturated with water. Thus when the run-off increases because of increased precipitation there is a drop in pH and an increase in the sulphate concentration of the run-off water. Based on a limited number of experiments in the field the authors tentatively conclude that the acidity of the rain affects the run-off directly during

heavy rains. However, with smaller amounts of precipitation the direct effect is difficult to detect.

The authors recognize that several sources contribute to the acidification of lakes and rivers. However, they conclude that changes in the composition of the precipitation during the recent decades, mainly because of increased combustion of fossil fuels, seem to be a dominant cause at least in some of the affected areas.

E. ACIDIFICATION OF SOILS BY ACIDIC PRECIPITATION - MARGINAL EXAMPLES

This section is a review of papers that report effects of "acidic precipitation" on soils. It is the opinion of the reviewer that many of the effects described in these papers are due to dry deposition and/or particulate air pollution not acidic precipitation.

(1) Nutrient Levels in Rainfall, Lodgepole Pine Foliage, and Soils Surrounding Two Sulfur Gas Extraction Plants in Strachan, Alberta.

by J. Baker In: Environment Canada Forestry Service, Information Report NOR-X-194, June 1977, 18 pp.

Analyses of rainfall, lodgepole pine tissue and soils were carried out on samples from control and SO_2 -impinged areas around two gas processing plants. Just the soil information will be presented here.

Soils samples were taken from the surface litter, 5 to 15 cm soil layer and the 15 to 30 cm soil layer of sandy and silty loam soils. Ca, Mg, Fe, Al, K, Na, S, P and pH analyses were performed.

The ionic composition of soil solutions and exchange complexes for the two general sample areas differed. Samples near the SO_2 source showed lesser amounts of basic ions (Ca, Mg, K, etc) and larger amounts of acidic constituents (Al, S, etc) even though the same general soil type prevailed over the entire study area. Based on these findings Baker feels that acidic precipitation (atmospheric SO_2) may be impoverishing the soils of bases but at the same time increasing the available soil Al and exchangeable acidity.

It should be emphasized that the SO_2 source, the Gulf Plant, had been in operation for 8 - 10 years prior to this study. Therefore, the establishment of an uncontaminated control area was virtually impossible. The control site, Radiant Creek, however, is protected by the Idlewilde Mountain.

(2) Acidity of Open and Intercepted Precipitation in Forests and Effects of Forest Soils in Alberta, Canada

J. Baker, D. Hocking and M. Nyborg; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 449-460

This article reports early field data on chemistry of rainfall from two

locations in Alberta affected by SO_2 emissions, and effects on forest soils from one of those localities. Preliminary laboratory studies by Baker showed that solution and transformation of S compounds in the soil are likely to greatly influence the solubility, mobility and distribution of soil minerals and nutrients.

Experimental sites were located at varying distances from SO_2 sources (Rocky Mountain House, Alberta, and Athabasca Soil Sands near Fort McMurray). Rainfall, stemflow, and throughfall were collected at weekly intervals and analyzed for their pH and S content. Snow was collected once from each site.

After two years of study, data showed that SO_2 appears to be having an acidifying effect on grossfall, stemflow, throughfall and soil solution at sites near major sources. The detail of the stemflow and throughfall studies will be presented in another section of this bibliography. Potassium chloride extractable acidity and aluminum are greater in soils suspected of SO_2 contamination while exchangeable bases are lower. According to the authors the acidifying effect of SO_2 at present is not as obvious on soil anionic constituents as that on soil cationic constituents.

(3) Smelter Pollution Near Sudbury, Ontario, Canada and Effects on Forest Litter Decomposition.

B. Freedman and T. Hutchinson; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds), Plenum Press, 1980, pp. 395-434

The authors explain that it is the purpose of this study to examine some of the effects of the large metal smelter near Sudbury, Ontario on the surrounding forested ecosystems. Present inputs of the major emitter pollutants to areas at various distances from the smelter and burdens of these pollutants in soils and vegetation will be monitored. In addition the effects of pollution in forest soils and litter decomposition will be studied in terms of i) litter study crop relative to rates of litter input; ii) populations of litter decomposers, and iii) activity indices related to rates of litter breakdown.

As an introduction Freedman and Hutchinson describe the environment of Sudbury and the smelting operation. Again it should be stressed that Sudbury represents an extreme condition of air and soil pollution and may not be related to what one would expect to find due to acid precipitation. Is is for this reason that the summarization of the findings of this 40 page paper will be kept to a minimum.

The studies were carried out along a SSE transect from the Coppercliff smelter. A map of the study area depicting the transect would have greatly complemented this study. Bulk deposition, and sulfation measurements were taken together. Soil was tested for heavy metals, bases, pH, organic Sulfur and

extractable S. Soil pH was measured on field wet samples by creating a slurry with distilled water. Peech (1965,918) cautions against the use of soil slurries as opposed to a 1:1 or 1:2 dilution as it increases the error of the liquid junction potential. Soil litter were collected through random sampling techniques. Soil CO₂ flux and soil acid phosphate assays were also determined. Soil microfaunal and microfungas populations were studied.

Results indicate that an accumulation of litter standing crop was occurring at forest sites close to the smelter and may be due to low mineralization rates. Lower rates of decomposition of leaves in litter bags occurred at contaminated sites, together with relatively low rates of soil metabolism activity. These include soil SO₂ flux and acid phosphatase activity. Lower populations of soil microfungi and microarthropods also occur. The author explains, however, that large within-site spatial variation was found. In a laboratory experiment involving the addition of Cu and or Ni to litter a depression of litter mineralization and SO₂ flux occurred at metal concentrations similar to those observed at contaminated sites in Sudbury.

The deposition of SO₂, and SO₄ in precipitation, forest litter and plant foliage were all elemental compared to the Coppercliff Smelter. However, there were no discernible distance to smelter related changes in bulk rainfall pH, soil litter pH, mineral soil pH or base leaching from litter in litter bags. Overall the authors conclude that "the negative effects attributable to acidic precipitation on terrestrial environments surrounding the smelter appear to be small, relative to the effects of SO₂ and heavy metal residences in soils".

(4) Effects of Acid Leaching on Cation Loss from Soils

T. Hutchinson; In: Effects of Acid Precipitation on Terrestrial Ecosystems T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp. 481-497.

In this study the leaching of a number of elements (Al,Mn,Fe,Zn,Ca and S) from soils in Smoking Hills (fumigated by intensive plumes of SO₂ from naturally occurring deposition of high S bitimunius shale) in the Canadian Arctic and from smelter polluted soils near Sudbury, Ontario are compared by analyses of stream outflow chemistry. The effect of controlled acid leaching on soils from these sites are compared. Both these sites are extreme conditions of soil pollution and results obtained through these studies may not be related to what one would expect to find due to normally-occurring acid precipitation, except after long time periods.

Water samples from the Smoking Hills area were taken along a stream 600m from the burning cliffs to a distance of 4 km. Samples were also taken from temporary pools. Soil samples were taken from the fumigated area and from an area 3.5 km away.

Samples of water were taken from a stream that drains a slag heap at Coniston. Soil was sampled at a relatively uncontaminated forest site 12 km west of the Copper Cliff smelters and from a site adjacent to the slag heaps. These soils were loosely packed into glass columns and leached with acid (pH 2.5, 4.5, 5.7).

Copper, nickel and aluminum in mineral soils close to the Coniston smelters were shown to be toxic to an array of bioassay species. Soils in the most intensively fumigated area of Smoking Hills were very acid (pH 2.2-3.0) and had high soil-S content. Ca and Mg appeared to be concentrating at depth in comparison to deeper soil just above permafrost and a control profile which were not base-depleted at the surface. The initial pH's of the soils used in the leaching experiment were 3.5 to 7.4 from the fumigated and control soils from smoking Hills; 3.3 to 3.6 from the polluted and relatively uncontaminated forest soils in Sudbury. The extremely low pH (3.6) from the so-called "uncontaminated" soil implies that this soil was in fact "contaminated". The soils initially yielded leachate having high elemental composition compared with later washings. The pH of the control soil leachate from Smoking Hills was greater than 7.0 when 15 l of pH 2.5 solution had been passed through the column. Only then did the pH drop, on the other hand, the soil from the fumigation zone lost large amounts of Al and Zn in all leachates.

The two Sudbury soils had low Ca concentrations in the leachates. These soils released small quantities of Zn. Mn, Fe, Al, Zn, Ca and Mg were present in high concentrations in runoff following rains and in tundra ponds in the acidified area near Smoking Hills. These elements have apparently been mobilized at low soil pH's.

The water analyses of the Smoking Hills area ponds (pH greater than 7.0) correlate with the acid soil leaching experiments, in that only low concentrations of Al, Fe, and Mn occurred in water samples. Similarly in the Sudbury area, where extensive SO_2 fumigation occurred with metal particulates emission, acidic streams carry high loads of clay metal elements as well as high concentrations of the metals emitted by the smelter.

Recently published data by G. Tyler dealing with Cu-Zn contaminated soils collected at a smelter near Gusum, Sweden were also discussed.

In summary, the mobilization and speciation of metals in soil or water appears to be strongly pH-dependent. At lower soil or percolate pH's the residence time of metals in soil is much shorter relative to higher pH's.

It is imperative when a large amount of data is being presented to the reader that the paper is well designed. Unfortunately it is the reviewer's opinion that the expanse of data was poorly arranged in this paper. The Sudbury Stream results were found in a separate section of the paper from the Smoking Hills stream results, making comparison difficult. The soil leaching experiments for both

Smoking Hills and Sudbury were presented together but unfortunately the author tended to discuss one soil and then the other and back again. At the beginning of the paper Hutchinson stated that soils would be leached with solutions of pH 2.5, 4.5 and 5.7 but only 2.5 and 4.5 data are presented with no further mention of the 5.7 leaching. Although there was obviously a great amount of time spent on this research project ie. field sampling, chemical analysis, and it appears to be quite thorough, the poor presentation of the results forces the reader to work through the paper in order to interpret the findings.

(5) The Effects of Acid Rainfall and Heavy Metal Particulates on a Boreal Forest Ecosystem near the Sudbury Smelting Regions of Canada

T. Hutchinson and L. Whitby; *Water, Air and Soil Pollution*, Vol. 7, 1977, pp. 421-438

Soil, vegetation and rainfall were sampled along transects from the Coniston smelter. The authors state that the soils were grey-wooded podzols (a term removed from the literature in the early 1970's and replaced by Gray Luvisol). Twenty-five sites were sampled.

Soil erosion had occurred on a large scale as a consequence of loss of vegetation. Metal accumulation in the soils was high; Ni 3000 ppm; Cu 2000 ppm in surface soils. The increased acidity of the soil (pH = 3.0) has increased metal mobility and solubility presenting phytotoxic problems. The metal binding of the organic fraction of the soil increased and high sulphur levels have been found in the fulvic acid fraction.

In conclusion the authors state that the "profound and damaging changes may be merely a consequence of the extreme conditions experienced at Sudbury or they may be a harbinger of things to come in many podzolic soils in areas of increasing acidity of rainfall". The reader should be clear on two points: 1) that the soils sampled were not podzolic soils but luvisolic and; 2) the conditions at Sudbury are extreme and are not representative of "true" acidic precipitation damages as much as they are of sulphur dioxide and particulate pollution.

(6) Effect of Sulphur Dioxide on Precipitation and on the Sulphur Content and Acidity of Soil in Alberta Canada

M. Nyborg, J. Crepin, D. Hocking, J. Baker; *Water, Air and Soil Pollution*, Vol. 7, 1977, pp. 439-448

Ninety-three fallout monitoring stations were installed in Alberta and

Western Saskatchewan. Rain was collected weekly over a 4 month period (1973-1974) at each station and snow was sampled at selected stations. Throughfall and stemflow were measured at eight sites in 1973 and 18 in 1974. Particulate fallout was measured at 11 stations (July-October 1974). The rate of SO_2 absorption by soils and pH depression was determined at all sites. One liter cartons of soil were placed under a roof at each station, all containers were watered. Similar soil containers were placed in the open, subjected to fallout, some with plants and some without plants. This study appears to be an expansion of the preliminary investigation outlined by Nyborg *et al* (1973).

The pH of soil in an area over 1000 km² from the gas plant under closed canopy was depressed at least 0.15 units over 3 months. pH depression in the forested sites is only half as great as that in prairie sites. The authors stress that considering cumulative pH depression over several years, forest soil may be seriously acidified. The amount of $\text{SO}_4\text{-S}$ gained by bare uncovered soil is up to 10 times as much as is detected in rainfall. Some soils store little or no $\text{SO}_4\text{-S}$ from S emissions, but instead convert $\text{SO}_4\text{-S}$ to forms that can be found in analysis for total S.

An experiment was conducted with a controlled chamber containing 24 ppb of SO_2 in the air. After 30 days of exposure two soils increased their $\text{SO}_4\text{-S}$ content by 8-9 ppm. Total S had increased by twice as much. The pH of the soils decreased by approximately 0.1 unit.

The results of the rain, snow, fallout sampling programs are presented in the body of the research paper but are not reviewed here. In conclusion the authors stress that the problem of soil acidification in Alberta by SO_2 emission is not all that simple because we do not know what proportion of emitted S is deposited as H_2SO_4 as compared to neutral salts. Soils are slowly acidified by SO_2 at a rate estimated at 1 pH unit in 10 to 20 years.

(7) Atmospheric Sulphur Dioxide: Effects on the pH and Sulphur Content of Rain and Snow; Addition of Sulphur to Surface Waters, Soil, and Crops; and Acidification of Soils

M. Nyborg and McKinnon, Allen and Associates Ltd.; Proceedings of a Workshop on Sulphur Gas research in Alberta. Environment Canada Forestry Service. Info. Report NOR-x-72 Dec. 1973 pp. 79-97

The objectives of this study were to find how and where sulphur dioxide comes to earth and in what concentrations. Specific objectives were to find out if sulfur dioxide emissions acidify precipitation, soils and waters in Alberta's

environment; and to determine the amounts of sulfur dioxide adsorbed directly by vegetation, soils and water at various distances from gas plants.

In 1972, 12 stations were established near the Shell water and gas plant. Rainfall and snow were sampled at each station in addition to experiments to determine the amount of S added to soils by emission and the effect of emission on soil pH.

The amount of S added to the soils was estimated by exposing a Gray Wooded (Gray Luvisol under present Canadian Classification System, 1976) topsoil of loam texture in 1 gallon plastic pots. After exposure for 3 months in 1972 the soil was analyzed for soluble $\text{SO}_4\text{-S}$.

In another experiment the Gray Luvisolic soil was placed in 2 gallon plastic pots, sown with vegetation and exposed at 10 stations without watering for almost 1 year (1973). Soil pH was determined on samples from 1 to 3 cm depth. In addition barley was grown on a slightly calcareous Dark Brown soil of loam texture in four 5 gallon pots for 4 months in 1972. They were watered periodically with distilled water. pH was determined in a mixture of 1 part soil and 2.5 parts water.

After exposure of the Gray Luvisols for 10 months, pH of the 1 to 3 cm depth was an average of 0.10 units lower at 5 stations downwind from a plant than at the 5 stations not directly downwind. The Dark Brown soils near the plant had a pH 0.06 units lower than the soil farther away from the S source. The authors state that although the pH differences are very small they were statistically significant, although what statistical test was employed is not mentioned. A problem with any pedological study is that the statistical methods used are likely more accurate than the soil data they incorporate. Also there are too few samples ($n=12$) for any valuable meaning to be given the statistical information obtained. The researcher has to use experience and informed judgement as well as careful examination of the size of scale, the size of sample, the nature of the variables and the circumstances of the study. In most cases very small differences, even though statistically significant, must be treated with skepticism.

Two exploratory experiments, one with poorly buffered subsoil and another with a black topsoil, also showed slight but consistent lowering of soil pH on exposure for 6 weeks directly downwind from the plant.

The results of preliminary rain, snow, water and vegetation experiments by the authors were not included in this review. In summary, Nyborg *et al* found that in Alberta S gas emissions are brought to earth through direct absorption by soils, vegetation and water, as well as by deposition in rain and snow. The amounts of S deposited in rain are very small, and the problem of acid rain is much less severe than in heavily industrialized parts of the world. However, the preliminary results did indicate that soils downwind from emission sources receive enough S through absorption to cause gradual lowering of soil pH.

(8) Effects of Sulphur Deposition on Litter Decomposition and Nutrient Leaching in Coniferous Forest Soils

T.M. Roberts, T. Clarke, P. Ineson, T. Gray; In: Effects of Acid Precipitation on Terrestrial Ecosystems, T. Hutchinson and M. Havas (eds.), Plenum Press, 1980, pp. 381-393

It has been hypothesized that acid rain may affect forest productivity by decreasing litter decomposition and thereby reducing the rate of nutrient cycling. An experimental field site was set up in 1977 at Delamere Forest in central England and studies of the sulphur cycle and effects of acid applications are now underway. The vegetation is a 50 year old Pinus sylvestris/Pinus nigra stand planted on a podzol with low cation exchange capacity and base saturation.

Precipitation was collected in the open and beneath the pine canopy and a lysimeter trench was built in a clear felled area adjacent to the pine stand. Daily SO_2 concentrations were measured. Nitrate/nitrite, pH, ammonium, phosphate, sulphate, Cu and Mg, Na and K were measured in both precipitation and soil. Only the findings of the soil experiments will be discussed here.

There was appreciable S enrichment beneath the canopy and further enrichment occurred beneath the organic horizons due to the dry deposition of SO_2 or mineralization of organic sulphur. There was some immobilization of ammonium in the L-layer in the open lysimeters. There was considerable mineralization of ammonium in the F and H layers in the open and beneath the canopy. There was no indication of nitrification in the L-layer or organic layer lysimeters. Ca enrichment occurred in the L-layer leachate and there was no further mobilization of Ca from the mineral layers. K was leached from the organic horizons and released from the mineral horizon.

Another part of the study was designed to examine the effects of acid treatments (pH 2.7-3.1) applied at a rate of 5 mm every two weeks on nutrient leaching and litter decomposition.

The acid application increased the acidity of leachates from the L-layer lysimeter but there was no effect on soil monolith leachates. These observations agree with Wiklander (1973/74) that acid rain is unlikely to further acidify strongly acid soils. Added sulphate was fixed in the mineral horizon likely due to adsorption by sesquioxides coatings on mineral particles. The acid application had no effect after the first 6 months on the rate of Ca, K, Na and Mg leaching from the soil. Abrahamsen et al (1976) found that acid solutions (pH 2, 3, 4, 6) applied to a Norwegian podzol over a two year period resulted in increased leaching of K, Ca, Mg and Al.

The authors conclude that episodes of acid precipitation with pH's around 3-

3.5 may produce small changes in the rate of pine litter decomposition and nitrogen availability. The effects of these changes on forest productivity cannot be quantified.

REVIEWS AND GENERAL PAPERS ON ACIDIC PRECIPITATION AND ITS EFFECT ON TERRESTRIAL ECOSYSTEMS

Since acidic precipitation became topical in the 1970's a number of reviews and bibliographies on this subject have been published. Outlines and comments on these reviews are found in this section. In addition there are an abundance of papers written on acidic precipitation and effects on the terrestrial ecosystem of a very general nature. None of these papers presents original research. Mainly they consist of reviews of the literature or aspects of acidic precipitation such as emission and sources or precipitation chemistry and transport, health effects and visibility problems. However, all the papers briefly mention some aspect of acidic precipitation and the terrestrial ecosystem.

(1) Acid Precipitation - Effects on Forest Ecosystems

G. Abrahamsen; Ecological Bulletin (Stockholm), Vol. 21, 1976, pp. 79-86

The objectives of the SNSF project are summarized as attempting to establish the effects of acid precipitation on forests and freshwater fish by investigating the effects of the pollutant on soil, vegetation and water.

Forest growth was examined via tree ring analysis. Regions of different acid precipitation regimes were compared as were intra-regional sites supposedly differing in sensitivity. No reduction in growth has been observed which is attributable to acid rain. Differences in climate, soil and silviculture practice reduce the sensitivity of the analytical method.

The possible effect on forest growth is likely to be a slow process affecting nutrients in soil with the possibility of accelerating the leaching of nutrients from the canopy. The observed higher concentration of chemical constituents in throughfall was felt to be the result of wash-off of dry deposition.

Experiments involving application of artificial rain to forest plants and soil lysimeters are introduced. Some results from soil studies are included. (These are reviewed elsewhere).

Experiments with seed germination and seedling establishment indicated a negative influence of soil acidity.

This paper is primarily a summary of the SNSF FR 2/75 report (Abrahamsen et al 1977).

(2) Report from the International Conference on the Effects of Acid Precipitation in Telemark, Norway, June 14-19, 1976.
Anonymous; *Ambio*, Vol. 5, 1976, pp. 200-201

The proceedings of the conference were published in the journal *Ambio* and relevant papers have been summarized in this bibliography. This issue of the journal also contained a summary of the proceedings where individual topics were addressed among which were effects on forest ecosystems.

Since forest productivity is related to base saturation of the soil, acidification will reduce soil fertility and reduce productivity. Field and laboratory experiments have found that acid precipitation may a) reduce microbial activity; b) affect nitrogen mineralization; c) accelerate mineral leaching; d) affect seed germination and seedling establishment; 3) accelerate cuticular erosion; f) enhance leaching of foliar nutrients; g) decrease pathogen, saprophyte and symbiont activity; h) induce leaf damage (at pH 2.5-3.5).

Forest productivity declines have not yet been unambiguously ascribed to acid precipitation. Nutrients in the rain may offset harmful effects. It is also noted that the nature of forest canopy will change the precipitation chemistry during throughfall.

(3) Research Summary - Acid Rain

Anonymous; US EPA Office of Research and Development, EPA - 600/8-79-028, 1979, 20 p.

This report is in a glossy booklet and was prepared mainly for the general public. It briefly presents the theory of the formation of acidic precipitation, fundamental chemistry of acidic precipitation, long-range transport of air pollutants as well as a definition of pH. Sensitive areas of the United States are depicted on a map (p.5) based on soil, climate and vegetation information. This map is very general.

The research that the EPA is funding with regards to acidic precipitation is outlined. Information regarding the type of experiments they are doing, the addresses of the researchers themselves and the place of research is all provided. This is a very useful summation of some of the American work. Atmosphere modeling and monitoring stations in the United States are discussed. On the last few pages a list of acid rain related research programs in the United States is provided. A few EPA publications and technical reports are listed along with the addresses one can write to obtain them. The names and addresses of 6 United

States scientists involved with acidic precipitation are provided. These include such people as N. Glass, G. Glass and P. Altshuller.

Although very general this booklet provides some useful and basic information about acidic precipitation to the general public as well as summarizing the EPA work on acidic precipitation and providing the addresses of scientists for those seriously involved in acidic precipitation research.

(4) A Bibliography: The Long-Range Transport of Air Pollutants and Acidic Precipitation

Anonymous; Ontario Ministry of the Environment and Atmospheric Environment Service, Environment Canada, 1980, 95 p.

References for 11 different aspects of acidic precipitation are presented in this bibliography. These topics are: emissions, sources and control; atmospheric chemistry; transport and deposition; networks; modeling; aquatic effects; terrestrial effects; health effects; material and structures effects; visibility and arctic haze; analytical techniques and methodology and miscellaneous. Only the section on Terrestrial Effects (6, pp. 71-88) will be commented on here.

The section on terrestrial effects is divided into three parts, 1) Soils and Geology; 2) Vegetation and Forests; and 3) Wildlife and Biological Indicators. References for 70 papers on soils and geology are presented. Many of the papers are strictly of a pedological nature and concerned with sulfate or nitrate movement in soil, or cation exchange capacity not acidic precipitation. In addition some of the papers are about SO_2 effects on local soils near a point source. Again, this is not acidic precipitation. However, the major papers on acidic precipitation and effects on soil appear to be listed in this section. Some more of the Norwegian SNSF work could be added. There are over 160 papers on Vegetation and Forests. A great number of them are on SO_2 and ozone effects on plants not acidic precipitation. Most of the more important references to acidic precipitation and the effect it has on vegetation seem to be noted. The third part on Wildlife and Biological Indicators has only 10 references. Again, most of them are not directly on acidic precipitation, but sulfur or other forms of air pollution.

(5) Acid Precipitation Causes and Consequences

H. Babich, D. Lee Davis and G. Stotzky; Environment, Vol. 22, 1980, pp. 6 -13 and 40 - 41

This article commences with a discussion of sources of acid precipitation precursors, atmospheric transformations and long distance transport. This is followed by a concise but relatively extensive review of the literature on environmental consequences. The authors emphasize the problem of extrapolation of laboratory experimental observations to real life predictions but note that many studies have demonstrated a relationship between long term low concentration exposures and short term high concentration exposures. The terrestrial ecosystem effects mentioned are summarized here.

Acidic precipitation may: 1) be neutralized by alkaline salts, 2) exchange for cations in soils, or 3) leach through soil and enter aquatic systems. Soil type is instrumental in determining susceptibility of an area. Soil with high cation exchange capacity can ameliorate detrimental effects, while acid podzolic soils are most susceptible to damage. (This contrasts with Wiklander's theory). Apart from the depression of soil pH, nutrient cations will be leached which in turn affects soil fertility. Mobilization of toxic heavy metals can also occur.

Simulation experiments using acidic solutions have shown a variety of plant responses. These include foliar lesions (at low pH, 3.0 or lower), reduced root development and growth, inhibition of seed germination in highly acidified soil and reduced fertilization in bracken fern via inhibition of spermatozoid motility. Soil microorganisms are adversely affected resulting in reduced litter decomposition and nutrient turnover rates and reduced nitrogen fixation rates. Host-parasite interactions are also affected. The lack of information regarding synergistic effects of acidic precipitation and other pollutants is noted.

This article continues with observations on adverse aquatic effects and on man-made materials. It concludes with some commentary on the uniqueness of acid rain as compared to its precursors. The gaseous precursors extend toxicity through their solubility products, such as bisulfite, sulfuric acid, nitrite and nitrous acid as well as H^+ ions. Acidic precipitation toxicity is primarily due to a pH effect.

Biological systems operate at an optimal pH and deviation from this optimum will have adverse effects. Examples cited include inhibition of enzyme activity, denaturation of proteins, reduced organism reproduction and population shifts to acid tolerant species.

This article is an excellent summary of the acid precipitation problem yet can be easily understood by the lay public.

(6a) Workshop Report on Acid Precipitation and the Forest Ecosystem

L.S. Doeringer and T.A. Seliga (eds); USDA Forest Service General Technical Report NE-26, U.S. Department of Agriculture, Forest Service, Upper Darby, PA, 1976, 18 p.

(6b) Acid Precipitation and the Forest Ecosystem: Report from the First International Symposium

L.S. Doeringer and T.S. Seliga; Journal of the Air Pollution Control Association, Vol. 25, 1975, pp. 1103 - 1105

(6c) Acid Precipitation and the Forest Ecosystem

L.S. Doeringer and T.S. Seliga; Bioscience, Vol. 26, 1976, pp. 564 - 565

During the First International Symposium on Acid Precipitation and the Forest Ecosystem held at Columbus, Ohio in 1975, a series of panel discussions were held where the session papers were summarized and integrated. The Workshop Report was prepared and released in which the various sub-topics of the symposium were considered. One of those sub-topics was "Effects on Forest Vegetation".

In addition, at least 2 other summaries of the symposium were published in scientific journals. The papers presented at the symposium were also published in the journal Water, Air and Soil Pollution. Relevant papers have been reviewed in this bibliography.

The report prepared by the panel on "Effects on Forest Vegetation" is summarized here.

Since vegetation covers most of the land surface of the earth, it is an initial deposition site for airborne material. Acidic precipitation will affect vegetation through the foliage or through soil-root interactions. Swedish researchers report a reduction in forest growth of 2% to 7% between 1896 and 1965 and attribute this to acidification. Similar studies in the United States have been inconclusive. It should be noted that the Swedish work referred to have been variously interpreted and is controversial. See Jonsson and Sundberg (1972).

Other reported effects of natural or simulated acidic precipitation include; alterations in cuticular features such as stomata size and frequency, increased bark acidity, changes in physiology of foliar organs, alterations in root functions, direct injury to tree foliage, accelerated nutrient leaching from foliage, inhibition or stimulation of pathogens and inhibition of nitrogen fixing bacteria.

Here it should be noted that some of effects noted are really SO_2 effects.

This workshop report also presents recommendations for future research.

This effort should attempt to identify specific organs, species, physiological processes or biological interactions that may be affected by acidic precipitation. Surveys to identify regions and types of vegetation most likely to be affected should be conducted in conjunction with precipitation monitoring programs. Integration with established watershed studies are desirable. Simulation experiments should be conducted to measure effects of acidity on injury, growth, physiology, biochemistry, pathogen interactions as well as other effects.

Ecological processes investigated should include nutrient cycling, changes in base exchange capacity of soils, nitrogen fixation, nutrient uptake, effect on microflora, mycorrhizae function, ecosystem diversity, soil-plant-animal interrelations and ecosystem stability.

If significant alterations are detectable, computer modelling may be useful to predict potential long-term effects.

(7) Acid Rain: Biological Effects and Implications

R.W. Ferenbaugh; Environmental Affairs, Vol. 4, 1975, pp. 745-758

This article is a summary of some of the real and potential effects of acid precipitation on biological and ecological systems. The nature and occurrence of acid precipitation are mentioned briefly. Effects of acid aerosols on mammals and acidification of aquatic systems are discussed.

Implications to the soil system consist of a reduction of nitrogen fixing capability since the blue-green algae responsible for fixation will not function below pH 6. Leaching of nutrients will also be accelerated. Plant productivity will ultimately be reduced. Forests can be susceptible if they occur on acidic soils with low buffering capacity.

The embryonic tissue of plants may be especially sensitive to acidic precipitation. Leaching of nutrients from plant tissues can also occur. Bleaching of chlorophyll will reduce the carbohydrate producing capacity of plants. Reproduction may be affected. Plants probably exhibit different degrees of susceptibility, depending on their morphology.

A reduction in plant productivity may have serious consequences to the forest products industry or to the production of food crops.

Some possible solutions to the problem are examined, ie., reducing SO₂ emissions, along with the repercussions of such control measures.

This article is written for a general audience and cannot therefore be a critical review of the literature. Much of the literature cited and relevant to effects of acid precipitation on soils and vegetation is summarized in this

bibliography.

(8) The Effects of Precipitation on Aquatic and Terrestrial Ecosystems: A Proposed Precipitation Chemistry Network
J.N. Galloway and E.B. Cowling; Journal of the Air Pollution Control Association, Vol. 28, 1978, pp. 229 - 235

Precipitation networks measuring the deposition of water from the atmosphere are well established. However, networks designed to measure the composition of precipitation water are few. This situation is improving.

Scavenging of atmospheric gases, aerosols and particulates by precipitation will determine precipitation composition and in turn can result in beneficial or deleterious effects on the environment. Nutrients in the precipitation can be a significant source of nutrients to terrestrial ecosystems where soil mineral weathering is slow or where the soil minerals are deficient in plant nutrients.

On the other hand, the increasing prevalence of strong acids resulting from fossil fuel combustion may have deleterious effects. The work of Jonsson and Sundberg (1972) is cited as reporting a 2 - 7% reduction in forest growth in Sweden between 1950 and 1965. The conclusions of the Swedish work are misinterpreted. Also summarized are a series of observations based on laboratory experiments with acidic solutions and vegetation. These include foliar injury, poor seed germination, accelerated foliar leaching, increased erosion of epicuticular waxes, decreased nitrogen uptake, various alterations in host parasite interactions and reduced nodulation and nitrogen fixation by legumes.

This paper continues with a review of the dependence of aquatic systems on precipitation inputs and a discussion of aquatic sensitivity to acidic precipitation. It concludes with a call for a systematic study of precipitation chemistry in North America and some suggestions for standardization of techniques.

(9) A National Program for Assessing the Problem of Atmospheric Deposition (Acid Rain), (A Report to the Council on Environmental Quality)
J. N. Galloway, E. B. Cowling, E. Gorham, W. W. McFee; National Atmospheric Deposition Program, NC-141, Dec. 1978, 94 p.

This is a report by environmental scientists to the executives of the National Atmospheric Deposition Program, U.S.A.

The first 10 pages provide an introduction to the acid precipitation problem

in the United States, specifically. Background to acid rain, chemistry, recommended research programs and budgets are included in this section. The remainder of the report is a more detailed summary of established facts and research recommendations and a more fully annotated review of the current knowledge of acid precipitation and aquatic ecosystems, effects on soil and vegetation and effects of acid deposition upon aquatic ecosystems.

McFee (pp.64-73) discussed soil acidification due to acid precipitation and its associated effects. The information provided is similar to that in his paper (McFee, 1980) which was reviewed in this bibliography. McFee provides a general and comprehensive review of the literature on acid precipitation and soils. Eight "priorities for future research" are listed and among them are such suggestions as; further study of microorganisms; classifying susceptible soils, soil-metal availability and movement; definition of toxic levels of metals in soils; mapping of vulnerable areas; and studying soil weathering effects. Table 7 (p. 28) in the original text provides a list of research recommendations regarding soils, their priority level and the amount of money allocated for the study.

McFee and Gorham discuss (pp. 74-82) soils in terms of materials leached and materials retained under an acid precipitation regime.

As well as providing an excellent summary of acid precipitation and effects on soil, this report includes a review of the most prominent papers on the subject and an indication of where research on soils and acid precipitation is headed in the U.S.A.

(10) The Effects of Acid Precipitation on Aquatic and Terrestrial Ecosystems
 J. Giddings and J.M. Galloway; In: Literature Review on Acid Precipitation, The Centre for Environmental Quality Management, and the Water Resources Sciences Centre, Cornell University, Pub. #EEP-2, 1976, pp. 1-40

The authors comment that the literature on the effects of acid precipitation on terrestrial ecosystems at this time (1976) was sparse and that few investigations had the luxury of baseline data with which to compare their results. Particular attention was given to inadequacies in present knowledge and recommendations for future research were presented based on the knowledge of acid precipitation at the time of this report.

The soils information reviewed came from three major sources; 1) lysimeter studies; 2) field observations; 3) stoichiometric models. At this time, according to the authors, there was no useful information on the effects of acid rain on soil microorganisms and decomposition processes. Mobilization of toxic metals had not

yet been investigated, either. Approximately 25 papers on the effect of acid precipitation on soils were reviewed by Giddings and Galloway. The majority of the papers presented in this 1976 review are discussed in greater detail in this bibliography. Some of the papers reviewed by Giddings and Galloway describe the effects of SO_2 or other air particulates on the soil not effects due to acid precipitation.

Experimentation by simulated acid rain application to plants has been conducted by various researchers. Some observations include reduced growth, leaf damage, death of leaves in plants, alteration of chemical composition of tissues, increased leaching, decreased chlorophyll content and decreased productivity. Lichens and mosses appear especially sensitive to acid rain treatments. Effects on forest productivity have not been conclusively demonstrated.

A table listing plant species supposedly tolerant to acid precipitation is given but it should be pointed out that this listing in fact refers to SO_2 tolerance. Some recommendations for further research include: 1) additional experimentation with acid applications to soil-plant systems; 2) determination of long-term effects on chlorophyll, nutrient balance, productivity and tissue chemical composition; 3) determining pH thresholds for direct acid damage; 4) examination of plant-soil-microorganism interactions of continued monitoring of forest productivity; 5) standardization of experimental design for effects of acid precipitation on plants.

(11) Effects of Acid Precipitation

N.R. Glass, G.E. Glass and P.J. Rennie; Environmental Science and Technology, Vol. 13, 1979, pp. 1350-1355

The sources, nature, occurrence and effects of acid precipitation are addressed in this publication. The effect of acid precipitation will depend on the nature and properties of the impacted materials. Calcareous soils of the Canadian prairies or southern Ontario are not of concern. Podzolic soils of eastern Canada are deficient in nutrient elements and display natural acidities.

Aquatic sensitivity to acid input is discussed. It is dependent on the neutralizing capacity of the water which in turn is related to the characteristics of the watershed.

Soil effects which are of concern include acidification, calcium removal, aluminum and manganese solubility and useful microorganism elimination. Some acid podzolic soils may resist further pH depression by loss of bases. It may be possible to map sensitive soils on the basis of exchangeable calcium status. Leaching of lysimeters and monitoring calcium release may approximate soil

changes under field conditions.

Vegetation may be affected directly, via foliage, or through changes in the soil. Necrosis of tissue which has been observed at a pH below about 3 may decrease productivity. Foliar losses of nutrient cations have also been shown to increase with increasing acidity. Changes in nutrient cycling may depress soil fertility. Host parasite relations may be affected.

There is every indication that acidic precipitation is deleterious to vegetation. A program to assess the affect to major crops has been undertaken by the U.S. E.P.A.

While this publication does not contain a reference list, a mimeographed report version of the text does. Most of the relevant references are reviewed in this bibliography.

(12) A Brief Summary of the Sensitivity of the Environment to Acid Precipitation
N.R. Glass, C.F. Powers, J.J. Lee and D.L. Rambo; US EPA Report (Draft), US
EPA Environmental Research Laboratory, Corvallis, Oregon, 1980.

This report is a summary of recent US EPA research project reports addressing effects of acid precipitation and attempts to identify sensitive areas.

Hendrey et al (1980) have mapped the bedrock geology east of the Mississippi River and designated sensitive areas on the basis of buffering capacity of the bedrock.

McFee et al (1980) delineated sensitive areas of the eastern USA on the basis of soil buffering capacity (CEC), base saturation, management practice and carbonate abundance.

Lee et al (1980) have conducted simulated acid rain experiments using 35 crop plants and assessed foliar injury and yield at various levels of acidity.

Lee and Weber (1980) have examined incident and throughfall rain, litter leachate chemistry in forests, the role of a forest in affecting changes in precipitation chemistry and nutrient cycling.

Summaries of these reports are presented in this bibliography (and will be included as the reports become available).

(13) Effect of H^+ Ion Activity and Ca^{++} on the Toxicity of Metals in the Environment

T.C. Hutchinson and F.W. Collins; Environmental Health Perspectives, Vol. 25, 1978 pp. 47 - 52

Various aspects of the relationships between acidic soils and plants are reviewed in this paper. Special emphasis is placed on the increased solubility of toxicity of heavy metal elements associated with acid soils. The role of Ca^{++} in ameliorating such deleterious effects is also discussed.

A brief discussion of the effects of acidic precipitation on soils reviews some literature. Such include increased leaching of Ca and Mg with accompanying decrease in base saturation, mobilization of Al, Mn and Fe, a possibility of structural changes in humic acids and toxicity of soluble heavy metals.

The repercussions of aquatic system acidification are also discussed.

(14) The Influence of Rainfall Composition on the Yield and Quality of Agricultural Crops

J.S. Jacobson; Paper presented at International Conference on the Ecological Impact of Acid Precipitation, Sandefjord, Norway, March 11-14, 1980, (draft)

The effect of precipitation containing elevated concentrations of H^+ or other ions and other organic and inorganic substances is still ill-defined. Compounds in rain may affect vegetation by direct contact or by inducing changes in the soils. This paper reviews the current state of knowledge on the direct contact effects of contaminants in rainwater.

Plant cells regulate their internal pH by transport of H^+ ions and through enzymatic reactions so as to maintain physiologically optimum conditions. The capacity of cells to maintain pH at desired levels may be a genetically determined factor controlling susceptibility of plants to injury by acidic precipitation. Acidification of cell walls loosens chemical bonds and may account for observations of abnormal cell elongation and proliferation in simulated acid rain experiments.

Absorption or leaching of elements from aqueous solutions can occur into or from foliage. Physical, chemical and morphological characteristics of the leaf surface and composition of the rain will regulate this exchange. Exchange of ions in foliage with H^+ ions in rain may lead to nutrient deficiencies, alter nutrient flows in the ecosystem and lead to changes in leaf surface microflora. However, experimentation with the role of rainfall acidity and foliar leaching losses have not

been able to demonstrate decreases in nutrient content of foliage. Stimulated root uptake may be controlling foliar composition.

Plants may possess characteristics which provide mechanisms of tolerance to acidic rain. Leaf shape, orientation and surface characteristics may prevent liquid contact with the leaf surface. Physical, chemical, mechanical and morphological characteristics together with a capacity of biochemical and physiological systems for buffering acidity will determine tolerance. Specificity of pollination mechanisms can also predispose plants at this stage of the life cycle to harm.

Experimental approaches to the study of effects of rainfall composition on vegetation have employed a variety of techniques and conditions. Results of some recent experiments are provided in table form. These refer to occurrence of foliar symptoms and changes in growth and productivity and suggest that greenhouse grown crops are more susceptible to acid solutions in terms of growth and yield. Sulphate and nitrate concentration and interactions with gaseous pollutants affect response.

Positive effects of acidic precipitation may be caused by the nutrient characteristics of nitrate and sulphate or changes in soil properties may increase nutrient availability. Acid induced changes in photosynthate partitioning may also lead to increased yield.

Research on the influence of rain composition on plant growth and yield is at an initial stage. Careful attention to procedures for simulation experiments is necessary. Consequences for long-range agricultural productivity requires knowledge of changes in soil fertility as well as dry deposition of pollutants.

(15) Impacts of Air Pollution on Forest Ecosystems

T.T. Kozlowski; Bioscience, Vol. 30, 1980, pp. 88 - 93

This article is a general review of the effects of air pollution on vegetation at the organism and community level. SO_2 and O_3 are the primary pollutants discussed.

Acid rain is also addressed, beginning with a description of the general phenomenon. There is also a brief, one paragraph, summary of effects on vegetation based on simulation experiments conducted by other researchers.

(16) Acid Precipitation

J.R. Kramer; In: Sulphur in the Environment, Part I, The Atmospheric Cycle
J. O. Nriagu (ed) John Wiley and Sons Inc., New York, 1978, pp. 325-369

This chapter is a general introduction to acid precipitation and is primarily a review of the literature. The publications concerning vegetation and soil effects are reviewed individually and more extensively in this bibliography.

The formation and occurrence of acidic precipitation and ecological processes which may be affected by acidification are discussed. A review of the literature dealing with acidification of aquatic systems and soils and effects on vegetation is also given.

Vegetation effects mentioned include growth abnormalities, increased foliar cation leaching, chemical alterations of canopy throughfall, forest production changes, litter decomposition rate reduction and reduced seedling establishment.

In two pages Kramer very briefly reviews papers on such topics as the acid nature of soils due to atmospheric deposition of SO_2 and SO_4 ; susceptible soils and overall reaction to acid deposition, soil leaching studies of metals and rate of leaching in soils due to increased H^+ input.

(17) Acid Precipitation

G.E. Likens; Chemistry and Engineering News, Nov. 22, 1976, pp. 29-44

The chemical nature, occurrence and sources of the acidity in precipitation is presented along with some observation on how the areas receiving the acid rain are expanding. Some observations on the effect of acid precipitation on terrestrial ecosystems are included.

It is noted that effects on the terrestrial ecosystems are difficult to interpret since these are highly complex and subject to a variety of environmental variables. Laboratory and field experiments indicate that acid rain can increase leaching of nutrients and organic substances from foliage, accelerate cuticle erosion, cause leaf damage when pH falls below 3.5, alter response to associated pathogens, symbionts and saprophytes, affect germination of seeds and establishment of seedlings, affect nitrogen availability, decrease soil respiration and leach ions from the soil.

A critical factor which may have been overlooked in studies of effects on vegetation is the sensitivity of specific life stages. Germination, flowering, fertilization and breaking of bud dormancy may be such sensitive stages and the occurrence of a particularly acidic rain event may result in a poor food crop.

While emphasis has been on H_2SO_4 , the occurrence of HNO_3 in rain may be masking adverse effects by supplying nutrient nitrogen to forests.

Continued research is fundamental to evaluating the severity of the problem.

This publication may be regarded as a general synopsis of the acid precipitation issue.

(18) Acid Rain: A Serious Regional Environmental Problem

G.E. Likens and F.H. Bormann; Science, Vol. 184, 1974, pp. 1176-1179

Acidity of precipitation falling over the N.E. United States has been increasing in recent decades. Such changes are due to increased combustion of fossil fuels emitting acid precursors to the atmosphere. However, this increased acidity has been accompanied by decreases in the sulphur content of precipitation. It appears that a shift from coal to natural gas combustion has favoured the formation of HNO_3 while removal of particulates from stack gases has also removed neutralizing agents.

The effects to ecosystems of this increased acid input is largely unknown but potentially manifold and complex. A brief summary of the literature points out some of the potential effects to terrestrial ecosystems. Such effects are reduced forest productivity, necrosis of foliage, reduced pollen germination and pollen tube growth, leaching of foliar nutrients and erosion of cuticles which can predispose plants to pathogen attack. Increased leaching of soil cations represent added stresses to the ecosystem.

Some of the observed effects to aquatic ecosystems are also mentioned.

This paper is a general summary of the acid rain problem. The literature cited and addressing terrestrial effects are reviewed more extensively in this bibliography.

(19) Acid Rain

G.E. Likens, F.H. Bormann and N.M. Johnson; Environment, Vol. 14, 1972, pp. 33-40

This paper discusses the emission, transport and deposition of acidic substances from anthropogenic sources. Observations of decreasing precipitation pH over various places in the world are described.

The ecological effects may be manifold and very complex, including increased leaching rates of nutrients from plants and in soil, aquatic acidification

and effects on organism metabolism. Synergistic reactions with other air pollutants are also possible.

Possible losses of nutrient elements from the soil, such as calcium, may not result in short-term damage to arable land, but may necessitate capital cost to replace such nutrients. A possible reduction in forest productivity in Sweden is mentioned also.

Observations on the temporal changes in aquatic chemistry are discussed.

(20) Biogeochemistry of a Forested Ecosystem

G.E. Likens, F.H. Bormann, R.S. Pierce, J.S. Eaton and N.M. Johnson; Springer-Verlag, New York, 1977, 146 p.

This publication is a compilation of the research conducted at the Hubbard Brook Experimental Forest in New Hampshire. This project was designed to examine the functioning of a small ecosystem and during the course of the study precipitation was collected and found to be acidic. The acidity was increasing with HNO_3 responsible for the increase while H_2SO_4 remained the dominant acid in the precipitation.

Investigations on the effects of acid precipitation on the forest ecosystem undertaken in conjunction with this project have been summarized elsewhere in this bibliography. A brief reference to this work is made in this publication. Increased foliar leaching of cations with increasing H^+ ion content of precipitation, reduction of nitrogen fixation or nitrification in soils, leaching of CaCO_3 from soil, reduced forest productivity or reduced resistance of plants to pathogen attack are cited. Cumulative effects over a number of years may result in a deterioration of the forest ecosystem as a result of acid precipitation together with the wide array of other pollutants.

(21) Acid Rain

G.E. Likens, R.F. Wright, J.N. Galloway and T.J. Butler; *Scientific American*, Vol. 241, 1979, pp. 43-48

This publication is a general synopsis of the acid rain phenomenon. It addresses atmospheric chemical reactions, transport, increasing precipitation acidity in Europe and the US, monitoring efforts and control measures.

Effects on aquatic systems are addressed. Terrestrial vegetation may be being affected because the acidity required to produce damage in laboratory

studies is being met under ambient conditions, especially during the initial stages of a rainfall event.

It should be pointed out that while acidity of the initial part of an event may be sufficient to cause damage in laboratory experiments, the duration of such extreme acidity would be insufficient under ambient conditions.

(22) Effects of Airborne Sulphur Pollutants on Plants

S.N. Linzon; In: Sulfur in the Environment: Part II, Ecological Impacts, J.O. Nriagu (ed), John Wiley & Sons Inc., New York, 1978, pp. 109-162

This article consists primarily of a literature review and the author's experience on the effects of SO_2 on plants and forest ecosystems. The brief review of the literature regarding acidic precipitation effects on vegetation addresses the question of forest productivity changes.

Assessments of the changes in forest growth as a result of acidic precipitation have been inconclusive. Variability of tree growth due to site differences, competition, tree age and genotype together with the beneficial effect of NO_3^- (in rain) fertilization are cited as reasons for the uncertainty.

Alteration of host-parasite relations, cuticular erosion, nutrient cation leaching, plant growth changes and increased cadmium uptake are cited from the literature when simulated acid rain experiments are described.

It is expected that unless the proliferation of acidic precipitation is curtailed, forested regions in susceptible areas may be degraded. Crop plants should not be affected as much due to intensive management practices ameliorating negative effects of acidic precipitation.

This chapter is primarily concerned with SO_2 and vegetation. The acidic precipitation literature reviewed is summarized in this bibliography.

(23) Acid Precipitation: Impacts on the Natural Environment

L.N. Overrein; Paper presented at: The Sulphur Gas Research Conference, University of Alberta, Canada, Nov. 17-18, 1977

Various aspects of acidic air pollution are considered including sources, transport, deposition and effects. The effects of acid precipitation on plants and soil are discussed briefly.

While forest productivity declines have been noted in southern Scandinavia and the N.E. United States, the cause cannot be linked unequivocally to acid

precipitation. Experiments have shown that acid precipitation can leach inorganic and organic substances from foliage, accelerate cuticular erosion, produce leaf damage at pH below 3.5, alter response to pathogens, symbionts and saprophytes, affect conifer seedling germination, affect nitrogen availability in soil and increase leaching of nutrients from soil.

The author further notes that plants may be especially sensitive to acid precipitation at certain stages of the life cycle. Germination, flowering, fertilization and breaking of bud dormancy are such sensitive stages. If an acid event occurred during such stages of crop plants, a poor yield would result. Vegetation would be directly affected by such an event while aquatic systems would be capable of diluting the acid.

Nitrogen in precipitation may be masking deleterious affects of acidity on forests. This problem deserves further study.

(24) Acid Precipitation in Atlantic Canada

R.W. Shaw; Environmental Science and Technology, Vol. 13, 1979, pp. 406 -411

This report discusses the occurrence of elevated concentrations of sulphate in the air and in precipitation in Atlantic Canada. It is contended that air parcels carry pollutant laden air over great distances and result in temporal fluctuations in sulphate loading.

The implications of environmental acidification are briefly mentioned by referring to studies documenting deleterious effects to aquatic ecosystems.

Some potential effects on the terrestrial ecosystem mentioned include nutrient leaching from soil, creation of unsuitable habitat for nitrogen fixing microorganisms and the possibility of forest productivity decline. It is also stated that since most of the soils in the Atlantic region are acidic podzols, whose productivity is dependent on pH, acid precipitation may have an adverse effect.

(25) Acidic Precipitation and Forest Vegetation

C.O. Tamm and E.B. Cowling; Water, Air and Soil Pollution, Vol. 7, 1977, pp. 503-511

Vegetation is capable of taking up substances from the atmosphere via the foliage. These may be beneficial or detrimental. As chemical composition of rainfall changes in time within or between events, the effects will also vary. Acidic precipitation should be understood not only in terms of amounts of

substances yielding H^+ ions, but in terms of a balance between other ions dissolved in precipitation. A listing of potential effects of acidic precipitation on vegetation is given. Indirect effects mediated through the soil are excluded.

Direct effects include: 1) Damage to protective surface structures such as cuticle; 2) Interference with functioning of guard cells will alter gas exchange processes or provide pathways for pathogen invasion; 3) Poisoning of plant cells after diffusion of acidic substances through stomata or cuticle resulting in necrotic lesions; 4) Disturbance of normal metabolism or growth processes without necrosis of plant cells; 5) Alteration of leaf and root exudation processes may affect associated microorganism populations; 6) Interference with reproductive processes; 7) Synergistic interaction with other environmental stresses.

Indirect effects include: 1) Accelerated leaching of substances from foliar organs following cuticle damage; 2) Increased susceptibility to drought and other environmental stresses following disruption of cuticle and guard cell functions; 3) Alteration of symbiotic associations following changes in leaf and root exudation processes; 4) Alteration of host-parasitic interactions induced by increasing susceptibility to pathogens.

The authors proceed to discuss SO_2 effects on plants stressing the variable sensitivity of different species. Similar variability may also be expected to acidic precipitation. It is concluded that knowledge of effects of acidic precipitation on vegetation is inadequate.

It is important to recognize the differences between SO_2 and acidic precipitation and their effects on plants. SO_2 is a gas and therefore will have a different pathway of entry into vegetation than acidic water. Effects of SO_2 on vegetation in vicinities of point sources are well documented whereas acidic precipitation covers much wider regions far removed from emission sources. Lack of information on effects of acidic precipitation on vegetation predisposes authors to discuss SO_2 without stressing the differences in occurrence and properties of the pollutants.

(26) Acid Rain: An Emerging Environmental Problem

C.K. Varshney and L.S. Dochinger; Current Science, Vol. 48, 1979, pp. 337-340

This paper is review of the acid precipitation problem. It addresses such topics as sources, deposition and effects on various components of the ecosystem. Some of the points raised in the discussion of terrestrial affects are summarized here.

In the soil, acid precipitation may destabilize clay minerals, promote runoff,

reduce cation exchange capacity, promote chemical denudation, accelerate podzolization and dissolve and leach Ca^{++} , Al oxides and Fe hydroxides. Soil micro-organism populations may shift from bacterial to fungal dominance while nitrogen fixing organisms will also be affected. Metal toxicity to such micro-organism will also be a factor at low pH.

Vegetation alters incoming precipitation chemistry; forest canopies absorb H^+ ions. There is considerable species variation. Simulation experiments produce necrotic spotting and yield reductions, enhance cuticle erosion, alter pathogen response and affect seed germination and seedling establishment. Forest productivity changes have not been demonstrated as effects have not been severe enough to alter nutrient status appreciably.

The reference material used by the authors in this review has been summarized in this bibliography.

(27) Acid Precipitation in the Netherlands

A.J. Vermeulen; Environmental Science and Technology, Vol. 9, 1978, pp. 1016 - 1021

This report addresses mainly data on emission and deposition of acidic substances in the Netherlands. Energy production sources are discussed as responsible for the acidic substances. Prognoses for the future are offered.

A brief section also addresses ecological consequences. The type of soil in the Netherlands has a high buffering capacity. Reference to studies of lichens and mosses lead the author to conclude that this flora is being affected by acidic precipitation. It is also stated that leaching of soil takes place, leading to changes in vegetation.

This report does not contain citations; therefore it is impossible to determine the validity of such commentary on effects due to acidic precipitation. Other forms of pollution or disturbance may be responsible.

(28) Acid Precipitation - A Review

N.D. Yan; The Institute for Environmental Studies, University of Toronto,
Pub. #EE-9, August 1977, 35 p.

Although the majority of this review covers such topics as precipitation processes, precipitation chemistry, acid precipitation sources, sulphur depositions and Long Range Transport only the section forests and soils will be discussed in this

bibliography.

Yan begins his review by summarizing a number of sulphur dioxide papers rather than those on the topic of acid precipitation. Papers on the effects of acid precipitation on soil fertility and leaching rates are presented next. By 1978 there were a considerable number of papers on this topic while Yan presents only a few of these. Yan states that mobilization of toxic elements or reductions in nitrogen fixation will in the end, affect forest productivity.

POPULAR PRESS ARTICLES ON ACIDIC PRECIPITATION

A number of articles addressing acidic precipitation have appeared in newsmagazines, naturalist group publications and other publications which are aimed at the lay public. The authors of such articles examine the various aspects of the problem, including emission sources, transport, deposition and ecological effects. For the latter, aquatic aspects are stressed but terrestrial ecosystems are also mentioned. Researchers in the field are often interviewed and quoted. Aesthetic damage to the environment is usually emphasized.

The following lists such articles. Undoubtedly there are many others which have been overlooked.

1) Acid Rain Not Damaging Cash Crops

Anonymous

In: Cash Crop Farming, Jan. 1980, pp 32-33

2) Acid From the Sky

Anonymous

In: Mosaic, Vol. 10, No. 4, 1979, pp 35-40

3) Acid Rain: Scourge from the Skies

Collins, R.

In: The Reader's Digest, June 1980, pp 49-54

4) What Acid Rain Does to Our Land and Water

Dotto, L.

In: Canadian Geographic, Dec. 1979/Jan. 1980, pp 36-41

5) Acid Rain Fallout: Pollution and Politics

Gannon, J.

In: National Parks and Conservation Magazine, Oct. 1978, pp 16-21

6) Mounting Acid Rain

Glass, N.R.

In: EPA Journal, July/Aug. 1979, pp 25-27

- 7) The Acid Earth
A Harrowsmith Staff Report
In: Harrowsmith, Vol. 4, No. 22, 1980
- 8) The Deadly Toll of Acid Rain: All of Nature is Suffering
LaBastille, A.
In: Science Digest, Oct. 1979, pp 61-66
- 9) Acid Rain: Who Will Save Our Lakes?
MacGregor, R.
In: Maclean's, Vol. 93, No. 26, 1980, pp 40-44
- 10) Acid Rain
Martin, H.
In: Chinook, Summer 1979, pp 50-51
- 11) Acid Rain: Fossil Sulfur Returned to Earth
Nisbet, I.C.T.
In: Technology Review, Feb. 1979, pp 8-9
- 12) Forecast: Poisonous Rain
Rosenfeld, A.
In: Saturday Review, Vol. 5, No. 25, 1978, pp 16-18

SENIOR AUTHOR INDEX

Abrahamsen, G.	26,41,65,74,76,80,126,127,158	Horntvedt, R.	12,34
Alexander, M.	128	Hovland, J.	132
Andersson, F.	42	Hutchinson, T.C.	112,151,153,168
Anonymous	159,160	Irving, P.M.	12,45,46
Baath, E.	129	Ishac, Y.Z.	133
Babich, H.	130,161	Jacobson, J.S.	13,14,47,168
Bache, B.W.	77,112	Jeffries, D.S.	140
Baker, J.	28,66,149	Johnson, D.W.	89,113
Bjor, K.	29	Johnson, N.M.	114,141
Braekke, F.H.	78,130	Jonsson, B.	48
Bryant, R.D.	131	Kozlowski, T.T.	169
Cogbill, C.O.	43	Kramer, J.R.	142,170
Cole, D.W.	30,81	Kratky, B.A.	58
Cowling, E.B.	66	Lakhani, K.H.	35
Cronan, C.S.	30,82,83,136	Lang, D.S.	15
Crowther, C.	43,84	Lee, J.J.	22,23,49,68,90
Denison, R.	60,85	Lepp, N.W.	23
Dickson, W.	137	Likens, G.E.	170,171,172
Dochinger, L.S.	162	Linzon, S.N.	114,173
Eaton, J.S.	31	Malmer, N.	91,115,142
Evans, L.S.	3,4,5,6,7,56,57	Masaru, N.	59
Fairfax, J.A.W.	20,21,22	Matziris, D.I.	50,92
Ferenbaugh, R.W.	7,163	Mayer, R.	36,37,93
Freedman, B.	150	McColl, J.G.	38
Frink, C.R.	86,87	McFee, W.W.	93,116,117
Galloway, J.N.	164	Nihlgard, B.	39
Giddings, J.	165	Nilsson, S.I.	94,118
Glass, N.R.	166,167	Norton, S.A.	95,143
Gordon, C.C.	8	Nyborg, M.	153,154
Gorham, E.	138	Overrein, L.N.	96,144,173
Hagvar, S.	132	Pennay, R.A.	69,118
Haines, B.	68,87	Petersen, L.	97,119
Harcourt, S.A.	44	Reuss, J.O.	98
Henriksen, A.	139	Richter, A.	40
Hindawi, I.J.	10,11	Rippon, J.E.	99,134,144
Hoffman, W.A.	32	Roberts, T.M.	156
Hornbeck, J.W.	33,139	Robitaille, G.	70

Rosenqvist, I. 100,145
Scheider, W.A. 146
Schnitzer, M. 101
Scholz, F. 70
Seip, H.M. 102,147
Shaw, R.W. 174
Shen-Miller, J. 71
Sheridan, R.P. 16
Shriner, D.S. 17,61,62,63,102
Singh, B.R. 103
Skinner, R.G. 104
Sposito, G. 104
Tamm, C.O. 51,52,105,106,121,134,135,174
Tukey, H.B. 71
Tveite, B. 52
Tyler, G. 107
Ulrich, B. 108,122
Varshney, C.K. 175
Vermeulen, A.J. 176
Wedding, J.B. 17
Whittaker, R.H. 53
Wiklander, L. 108,109,122,124
Wood, F.A. 18,
Wood, T. 24,53,54,110
Yan, N.D. 176

1981
A56
06
1955-4
TD